CATALYSIS IN THEORY AND PRACTICE

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CATALYSIS
IN THEORY AND PRACTICE

BY

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PREFACE TO THE FIRST EDITION

In the development of chemical science during the preceding hundred years, the steady progress in importance which catalytic operations have achieved is distinctly remarkable. Their importance emerges alike in the purely theoretical and in the technical aspects of the subject. In the natural order, also, investigation has shown how predominating a part the catalytic phenomenon plays. From the strictly utilitarian point of view, Industry was not slow to appreciate the advantages to be derived from the employment of agencies which should facilitate and "speed-up" manufacturing processes, nor was there lacking a body of scientific workers who steadily supplied the investigative and theoretical bases upon which such applications could be reared. As the scientific viewpoint developed, the physiologist and biologist rapidly associated the simpler chemical phenomena with the more complex processes operating in living matter. To-day, therefore, catalysis intrudes prominently into all branches of natural science, both pure and applied.

The need for an exposition of the fundamental principles involved in this particular field of general chemistry and of the applicability of such principles in modern life has been widely felt and has offered to the authors the necessary inducement to prepare the present volume. An excellent chapter in Mellor's *Chemical Statics and Dynamics* has formed, hitherto, the sole treatment in English of the theoretical aspects of the problem. From time to time various papers have catalogued the more important practical applications of catalysis. The monograph of Sabatier, *La Catalyse en chimie organique*, deals more particularly with the applications to preparative organic chemistry, with slight reference to the physico-chemical theories involved. Dr. Gertrud Woker has compiled a detailed survey of the theoretical aspects of catalysis and of their application to the problems of analytical procedure, in Margosches's *Sammlung*, entitled, "Die chemische Analyse", vols. xi., xxi., and xxiii. The volume entitled *Unter-*

suchungen im Gebiete der Kinetik der chemischen Reactionen und Katalyse, by the Russian, Orloff, and *La Catalisis Quimica*, by P. E. Vittoria, are supplementary to the above volumes. From all these sources, to which we wish to acknowledge our indebtedness, we have freely drawn in an effort to obtain a systematic and comprehensive treatment of the whole subject

For personal assistance in the compilation of the work we wish to express our thanks to Professor F. G Donnan, F R.S, for advice and for stimulating and continuous encouragement, and to Professor W. M. Bayliss, F R S, for a kindly criticism of the chapter dealing with Ferments and Enzyme Action.

The diagrams have been drawn by our laboratory assistant, Mr. A. Hiscocks, to whom we express our acknowledgments and thanks

With a subject the literature of which is already so considerable and is increasing so rapidly and continuously, it is not possible to give an exhaustive summary of the scientific and technical references The aim, rather, has been to embody in the text the main lines of development, choosing from the available examples suitable data for the purposes of illustration It is hoped that such an object has been achieved Criticism or additional information relative to the subjects treated will be welcomed

The subject matter of the volume deals with the influence of catalysts in the reactivities of atoms and molecules among themselves. In the future, the problems of chemistry will centre more and more around the intra-atomic reactions and atomic structure Already, the evidence is available that the atoms undergo processes of radio-active disintegration at definite but, thus far, unalterable speeds. Will the catalytic agencies be found which shall accelerate the velocity of atomic decay and render available the enormous stores of intra-atomic energy? Such is a fitting problem for the years that lie ahead.

LONDON, *November* 11, 1918.

PREFACE TO THE SECOND EDITION

PROGRESS in catalytic studies since the first edition of this volume has necessitated a complete revision of the text and the addition of several new chapters.

Advances are recorded in both the theoretical and practical field. The concept of "active" molecules first postulated by Arrhenius is beginning to assume at least the shadow of an objective reality, and the processes of activation explored by the physicist are being earnestly sought for in chemical reactions. In contact catalysis, experimental investigations have yielded a definite concept of the solid catalytic agent, its properties and behaviour, all of which could only be surmised some years ago. In the domain of theoretical homogeneous catalysis, very definite progress in correlating the data of catalysis with the thermodynamic properties of solutions can be recorded, and a commencement has been made in the inquiry as to the conditions of stability of associated complexes and their electronic structure.

In the applied science, the record of a new, high-pressure, catalytic industrial process, the synthesis of methyl alcohol and motor fuels from water gas, will serve to show what further potentialities are latent in the field.

The character of the volume remains the same. No attempt is made to make of it an extensive bibliography of catalytic literature. The rapidity with which the science is growing practically makes that an impossibility. It aims to present a critical survey of the catalytic field from the standpoint of the theory of the subject. It is the belief of the authors that any extension of our theoretical knowledge will cause the practical application to be more readily achieved.

We welcome the appearance of a second edition of Sabatier's monumental work, *La Catalyse en chimie organique*, both in an original French and an amplified English translation. It forms a very valuable complement, we believe, to the present volume, which, we hope, will be of value also to the organic chemist, stressing as it does the theoretical aspects of the practical preparative data of Sabatier We also acknowledge our indebtedness to the Reports of the Committee on Contact Catalysis of the National Research Council, U S A., which have materially lessened our labours by their frequent surveys of problems with which we are here intimately concerned

We hope that, in the revised form, the book will receive as kindly a welcome as met our initial effort We wish here to acknowledge our indebtedness to many kind friends for suggestive criticisms and advice as to the content of this work. It is our hope that the volume may be a further incentive to research and development in a very fruitful field

LONDON, *December* 1925

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES

ABBREVIATED TITLE.	JOURNAL.
Abh. Akad. Wiss. Berlin	Abhandlungen der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Abh. d. Bunsen Gesellschaft	Abhandlungen der Bunsen Gesellschaft.
Ahrens Sammlung	Ahrens Sammlung.
Amer Chem. J.	American Chemical Journal.
Amer. J. Physiol.	American Journal of Physiology.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim.	Annales de Chimie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Physik	Annalen der Physik.
Arch. d. Sci. Phys. et Nat. Geneva	Archives de Sciences Physiques et Naturelles, Geneva.
Arch. Inst. Physiol.	Archives de l'Institut de Physiologie.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Beitr. chem. Phys. u. Path.	Beitrage chemische Physik und Pathologie.
Ber.	Berichte der Deutschen Chemischen Gesellschaft.
Biochem. Zeitsch.	Biochemische Zeitschrift.
B.P.	British Patent.
Bull. Acad. Sci. Cracow	Bulletin International de l'Académie des Sciences de Cracovie.
Bull. Acad. Roy. de Belgique	Académie Royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Bur. of Standards	Bulletin of the Bureau of Standards (U.S.A.).
Bull. des Sciences Technol.	Bulletin des Sciences et Technologie.
Bull. Soc. Chim.	Bulletin de la Société chimique de France.
Bull. Soc. Ind. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Chem. News	Chemical News.
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.

ABBREVIATED TITLE.	JOURNAL
Compt. rend. Soc. de Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
D.R.P.	Deutsches Reichs-Patent
Edin Phil. J	Edinburgh Philosophical Journal
F.P.	French Patent
Gazzetta	Gazzetta chimica italiana
Jahresber.	Jahresberichte über die Fortschritte der Chemie
Jahresber. Ges. vaterl. Kultur	Jahresbericht der schlesischen Gesellschaft fur vaterländische Kultur
J. Amer Chem Soc.	Journal of the American Chemical Society
J. Biol. Chem.	Journal of Biological Chemistry, New York
J. Chem. Soc.	Journal of the Chemical Society
J. f Gasbeleucht	Journal fur Gasbeleuchtung und Wasserversorgung
J. Gas Lighting	Journal of Gas Lighting
J. Ind. Eng Chem	Journal of Industrial and Engineering Chemistry
J Inst. Pet Tech	Journal of the Institute of Petroleum Technologists.
J. Physical Chem	Journal of Physical Chemistry
J pr. Chem.	Journal fur praktische Chemie
J. Russ Phys Chem Soc	Journal of the Physical and Chemical Society of Russia
Medd. K. Vetenskapsakad Nobel Inst	Meddelanden fran Kongl-Vetenskapsakademiens Nobel Institut
Monatsh.	Monatshefte fur Chemie und verwandte Teile anderer Wissenschaften
Petroleum Zeit	Petroleum Zeitung
Pflüger's Archiv	Archiv fur das gesammte Physiolgie des Menschen und der Tiere
Pharm J	Pharmaceutical Journal
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin)
Phil. Trans	Philosophical Transactions of the Royal Society of London
Physikal Zeitsch	Physikalische Zeitschrift
Pogg. Ann.	Poggendorff's Annalen der Physik und Chemie.
Proc. Amer. Gas Inst.	Proceedings of the American Gas Institute
Proc. Chem. Soc.	Proceedings of the Chemical Society
Proc. Paint Varnish Soc.	Proceedings of the Paint and Varnish Society
Proc. Phys. Soc. London	Proceedings of the Physical Society of London.
Proc. Roy. Soc	Proceedings of the Royal Society
Quart. J. exp. Physiol	Quarterly Journal of Experimental Physiology.
Rep. Brit. Assoc.	Report of the British Association for the Advancement of Science
Schweigger's Journ.	Schweigger's Journal für Chemie und Physik.
Seifenfabrikant	Der Seifenfabrikant.

Abbreviated Title.	Journal.
Seifen. Zeit.	Seifensieder Zeitung.
Sitzungsber. K. Akad. Wiss. Wien	Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wien.
Sitzungsber. K. Akad. München	Sitzungsberichte der Königlichen bayerischen Akademie der Wissenschaften zu München.
Soc. Tech. de l'Ind. du Gaz en France	Société Technologique de l'Industrie du Gaz en France.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Farad. Soc.	Transactions of the Faraday Society.
U.S.P.	United States Patent.
Virchows Archiv.	Virchows Archive.
Wied. Ann.	Wiedemanns Annalen der Physik und Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. f. Beleucht.	Zeitschrift für Beleuchtung.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seylers Zeitschrift für physiologische Chemie.

All temperatures, unless otherwise stated, are in Centigrade.

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CHAPTER I

EARLY HISTORY

THE conscious development of catalysis in chemical science dates from the co-ordination by Berzelius, in 1835, of a number of isolated observations made by various investigators in the early decades of the nineteenth century. Berzelius for many years contributed annually to the Swedish Academy of Sciences a report on the progress of the physical sciences during the preceding year. The communication of March 1835, subsequently published as the *Jahresberichte für Chemie*, 1836, contained, *inter alia*, a discussion of the researches of Mitscherlich[1] on the rôle of sulphuric acid in the preparation of ether from alcohol. It was shown by Berzelius that the results of this investigation possessed features common to several investigations of the most diverse character.

The argument as developed by Berzelius may be briefly summarised.[2] "Up to 1800, it was recognised that, besides the normal tendency of bodies to combine, heat and in some cases light could also act in the process of combination. Later, the influence of electricity was recognised, but it was soon seen that chemical and electrical affinities were the same thing, and that heat and light had no other action than to augment and diminish these affinities." A new type of force was involved, however, according to Berzelius, in a number of reactions. Thus Kirchhof had shown[3] that in the conversion of starch to sugar by means of dilute acids, the acid effecting the change remained unaltered. Thénard discovered hydrogen peroxide and showed that in presence of acids the substance was stable. With alkali, however, decomposition set in with evolution of oxygen, which was also facilitated by the presence of substances such as manganese, silver, platinum, gold, and fibrin.[4] Edmund Davy[5] demonstrated that, with finely divided platinum soaked in spirit of wine, ethyl alcohol was oxidised to acetic acid. In 1822 Döbereiner[6] showed that spongy platinum in the cold induced the spontaneous combustion of hydrogen and oxygen, and this observation was followed by the discovery of Dulong and Thénard[1] that gold, silver, and even glass possessed the same property if the temperature of these agencies was sufficiently raised. Finally, cites Berzelius, the researches of Mitscherlich show that the conversion of alcohol to ether was not dependent on the affinity of sulphuric acid for water, since by a proper adjustment of conditions the addition of alcohol to sulphuric acid resulted in the evolution of ether and water, the sulphuric acid therefore being analogous to the alkali of Thénard in the decomposition of hydrogen peroxide.

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[1] *Pogg. Ann.*, 1834, 31, 273.

[2] *Jahresber.*, 1836, 15, 237; *Ann. Chim. Phys.*, 1836 (ii.), 61, 146.

[3] *Schweigger's Journ.*, 1812, 4, 108.

[4] *Ann. Chim. Phys.*, 1818, 9, 314.

[5] *Phil. Trans.*, 1820, 100, 108.

[6] *Schweigger's Journ.*, 1822, 34, 91; 1823, 38, 321.

Berzelius therefore concludes: "It is then proved that several simple and compound bodies, soluble and insoluble, have the property of exercising on other bodies an action very different from chemical affinity. By means of this action they produce, in these bodies, decompositions of their elements and different recombinations of these same elements to which they themselves remain indifferent.

"This new force, which was hitherto unknown, is common to organic and inorganic nature. I do not believe that it is a force quite independent of the electro-chemical affinities of matter; I believe, on the contrary, that it is only a new manifestation of the same; but, since we cannot see their connection and mutual dependence, it will be more convenient to designate the force by a separate name. I will therefore call this force *the catalytic force*, and I will call *catalysis* the decomposition of bodies by this force in the same way that one calls by the name analysis the decomposition of bodies by chemical affinity."

The illustrations of catalysis cited by Berzelius in the memoir just quoted represented by no means an exhaustive list of the catalytic operations which had up to that time been used and studied. Obviously, many of the primitive arts involved unconsciously the application of Berzelius's "catalytic force." The production of wine, for example, by fermentation processes dates back to the ancients, though neither sugar nor alcohol appears to have been known, as such, to Pliny, Berthelot tracing back the rectification of alcohol from wine no further than the eighth century.[2] The production of acetic acid by fermentation of wine gave the ancients their earliest acid solvent. The manufacture of soap by the action of alkalis on fats also dates back to ancient times. Pliny[3] refers to "Sapo, Gallorum hoc inventum", and makes it probable that the Romans received from Gaul and Germany a product prepared from animal fat and the aqueous extract of ashes. Ether, which has been attributed to the Arabians, was certainly well known in the Middle Ages, being produced by the action of sulphuric acid on alcohol. The first exact knowledge of its preparation we owe to Valerius Cordus in the sixteenth century. The mineral acids were not known until the alchemical era, but the preparation of sulphuric acid by setting fire to sulphur admixed with saltpetre is the alchemical origination of the catalytic lead chamber process of sulphuric acid manufacture. The identity of the sulphuric acid obtained by the different methods of preparation from alum, from vitriol, and from sulphur and nitre was established by Libavius in the Iatro-chemical era, to whom is also to be attributed the first use of the term "catalysis" in a chemical treatise. In the table of contents of his treatise on Alchymia is to be found a section devoted to "Catalysis", but, according to Goldschmidt,[1] examination of the treatise itself fails to reveal anything corresponding with that implied in our modern use of the term. One cannot entirely dissociate the alchemist's search for the "philosopher's stone" from the modern search for suitable catalysts. George Ripple likened the stone to a ferment. The records of the efficacy of the philosopher's stone in the literature of alchemy suggest, moreover, the poisoning of catalysts with which, later, this volume will be largely concerned. Thus, Roger Bacon ascribes to the stone the power to transform a million times its weight of base metal into gold. The more audacious Raymond Lully cites the transformation of ten billion times its weight of base metal. But, with the decay of alchemy, the claims become more modest, or the poisoning effect becomes the more pronounced, for John Price, the last alchemist and gold-maker of the eighteenth century, is but able to chronicle an efficacy of thirty times and one of sixty times the weight of the stone.

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[1] *Ann. Chim. Phys.*, 1823 (ii.), 23, 440; 24, 380.

[2] *Ann. Chim.*, 1852 (vi.), 23, 433.

[3] *Hist. Nat.*, 28, 12.

Of researches prior to and in the early decades of the nineteenth century concerned with the operation of a catalytic agent and not included in the co-ordination of Berzelius, particular mention might be made of the following. Mrs. Fulhame[2] dealt with the influence of water on chemical reaction, more especially in the reduction of metallic oxides and in the oxidation of carbon monoxide, and clearly demonstrated the necessity for the presence of water, at least in traces, for the production of reaction. The researches of Döbereiner on the combustion of hydrogen and oxygen were preceded by the observations of Sir Humphry Davy[3] on the capacity of platinum wires or foil heated to below redness to promote the combination of oxygen with coal-gas, cyanogen, hydrogen cyanide, alcohol, ether, or naphtha. Erman[4] showed that platinum at a temperature of 50° was sufficient to ignite a mixture of hydrogen and oxygen. Döbereiner's work on the action of cold platinum introduced into the gases was rapidly followed by that of Turner[5] on the action of platinum in promoting the combination of hydrogen with chlorine and other gases, and his unsuccessful attempts to cause preferential combustion.

Impurities such as hydrogen sulphide, ammonia, carbon disulphide, ethylene, and ammonium sulphide were shown to inhibit the activity of platinum. "It was this inefficiency of the platinum sponge on the compounds of charcoal and hydrogen in mixture with oxygen, while it reacts so remarkably with common hydrogen, and also, though slowly, on carbonic oxide ", that suggested to Henry[1] " the possibility of solving by its means some interesting problems in gaseous analysis. I hoped more especially to be able to separate from each other the gases constituting certain mixtures, to the compositions of which approximations had hitherto been made, by comparing the phenomena and results of their combustion with those which ought to ensue, supposing such mixtures to consist of certain hypothetical proportions of known gases " And the conclusion is drawn that, " When the action of the platinum sponge was moderate, only the hydrogen and carbonic oxide were consumed, or at most the olefiant gas was but partially acted upon From the facts which have been stated, it appears that when the compound combustible gases, mixed with each other, with hydrogen, and with oxygen, are exposed to the platinum balls or sponge, the several gases are not acted upon with equal facility, but that carbonic oxide is most disposed to unite with oxygen, then olefiant gas, and, lastly, carburetted hydrogen By due regulation of the proportion of hydrogen it is possible to change the whole of the carbonic oxide into carbonic acid without acting on the olefiant gas or carburetted hydrogen " At a temperature of 170° it was further shown by Henry that " when carbonic oxide and hydrogen gases in equal volumes, mixed with oxygen sufficient to saturate only one of them, were placed in contact with the sponge, from the quantity of carbonic acid remaining at the close of the experiment it appeared that four-fifths of the oxygen had united with the carbonic oxide and only one-fifth with the hydrogen ", a remarkable result, which was also obtained when excess was used This extraordinary research represents in many respects a study of catalytic action of the most fundamental importance even at the present day

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[1] *Zeitsch. Elektrochem.*, 1903, 9, 736.

[2] *An Essay on Combustion*, London, 1794.

[3] *Phil. Trans.*, 1817, 97, 45.

[4] *Abh. Akad. Wiss. Berlin*, 1818–19, 368.

[5] *Edin. Phil. J.*, 1834, 11, 99, 311.

The genesis of the modern contact process of sulphuric acid manufacture dates also from the period prior to the Berzelian definition of catalysis. Phillips, a Bristol manufacturer of vinegar, patented[2] the use of platinum, whether of wire or sponge, for the oxidation of sulphur dioxide by means of air The process was employed at Lille by Kuhlmann in 1883, but was abandoned owing to loss of catalytic activity by the platinum, an inhibiting factor which was not satisfactorily overcome in technical practice until the dawn of the present century

It is to Faraday[3] that we owe a detailed inquiry into " the power of metals and other solids to induce the combination of gaseous bodies " and into " some very extraordinary interferences with this phenomenon ". The researches were initiated in the course of experiments to render efficient the hydrogen-oxygen voltameter, in which Faraday "was occasionally surprised at observing a deficiency of the gases resulting from the decompositions of water, and at last an actual disappearance of portions which had been evolved, collected, and measured. . . . It was found that this effect was not due to the escape or solution of the gas, nor to recombination of the oxygen or hydrogen in consequence of any peculiar condition *they* might be supposed to possess under the circumstances; but to be occasioned by the action of one or both of the (platina) poles within the tube upon the gas around them." It was established that the positive platina plate was more active than the negative, and that with the former, in addition to its rapid action on oxygen and hydrogen, a feebler action was exerted by it on mixtures of nitrous oxide and hydrogen. According to Faraday, mixtures of olefiant gas or carbonic oxide with oxygen, or of equal volumes of hydrogen and chlorine, were not affected by the prepared platina plate.

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[1] *Phil. Mag.*, 1825, 65, 269.

[2] B.P 6069/1831

[3] *Experimental Researches in Electricity*, 1849, 1, 165, 6th series, Nos. 564-659, "Everyman's Library", No. 576, pp. 84-111, *Phil. Trans*, 1834, 114, 55.

"Reverting to the action of the prepared plates on mixtures of hydrogen and oxygen, I found that the power, though gradually diminishing in all cases, could still be retained for a period varying in its length with circumstances. . . . The continuance of the action greatly depended upon the purity of the gases used. . . . The act of combination always seemed to diminish, or apparently exhaust, the power of the platina plate."

As a result of his inquiries Faraday concludes that it may be observed of this action, that, with regard to platina, it cannot be due to any peculiar, temporary condition, either of an electric or any other nature: the activity of plates rendered either positive or negative by the pole, or cleaned with such different substances as acids, alkalis, or water; charcoal, emery, ashes, or glass; or merely heated, is sufficient to negative such an opinion Neither does it depend upon the spongy and porous, or upon the compact and burnished, or upon the massive or attenuated state of the metal, for in any of these states it may be rendered effective or its action taken away. The only essential condition appears to be a *perfectly clean* and *metallic surface*, for whenever that is present the platina acts, whatever its form and condition in other respects may be; and though variations in the latter points will very much affect the rapidity, and therefore the visible appearances and secondary effects of the action, *i.e.* the ignition of the metal and the inflammation of the gases, they, even in their most favourable state, cannot produce any effect unless the condition of a clean, pure, metallic surface be also fulfilled.

"All the phenomena connected with this subject press upon my mind the conviction that the effects in question are entirely incidental and of a secondary nature; that they are dependent upon the *natural conditions* of gaseous elasticity combined with the exertion of that attractive force possessed by many bodies, especially those which are solid, in an eminent degree, and probably belonging to all; by which they are drawn into association more or less close, without at the same time undergoing chemical combination though often assuming the condition of adhesion; and which occasionally leads, under very favourable circumstances, as in the present instance, to the combination of bodies simultaneously subjected to this attraction. I am myself prepared to admit (and probably many others are of the same opinion), both with respect to the attraction of aggregation and of chemical affinity, that the sphere of action of particles extends beyond those other particles with which they are immediately and evidently in union, and in many cases produces effects rising into considerable importance, and I think that this kind of attraction is a determining cause of Dobereiner's effect, and of the many others of a similar nature."

It will be evident, therefore, that Faraday, in 1833, and prior to the co-ordination by Berzelius of the several examples of catalytic action, had clearly expressed a theory as to the mechanism whereby such action should occur The theory, it will be observed, confirms the viewpoint expressed by Berzelius in his later publication, that the catalytic force is not independent of the affinities of matter but only a new manifestation of the same.

The retardation caused by admixture of foreign gases on the combination of hydrogen and oxygen was also studied by Faraday, who found that "the order in which carbonic acid and these substances seemed to stand was as follows, the first interfering least with the action: nitrous oxide, hydrogen, carbonic acid, nitrogen, and oxygen". These did not prevent the action of the plates, "nor was the retardation so great in any case as might have been expected from the mere dilution of the oxygen and hydrogen" Faraday found that ethylene decreased the action of platinum more than did carbon monoxide, but this result was not confirmed by Henry[1], Bancroft[2] thinks this was probably due to some impurity in Faraday's ethylene. The retardation by carbon monoxide, however, is well confirmed by both investigators.

Of the explanation of retardation, Faraday writes. "The theory of action which I have given for the original phenomena appears to me quite sufficient to account for all the effects by reference to known properties, and dispenses with the assumption of any new power of matter. I have pursued this subject at some length, as one of great consequence, because I am convinced that the superficial actions of matter whether between two bodies, or of one piece of the same body, and the actions of particles not directly or strongly in combination, are becoming daily more and more important to our theories of chemical as well as mechanical philosophy. In all ordinary cases of combustion it is evident that an action of the kind considered, occurring upon

[1] *Phil. Mag.*, 1836 (iii.), 85, 329.

[2] *J. Physical Chem.*, 1917, 21, 755.

the surface of the carbon in the fire, and also in the bright part of the flame, must have great influence over the combinations there taking place."

The student of catalysis no less than, for other reasons, the student of electro-chemistry is deeply indebted to Faraday for this early orientation into the mechanism of catalytic action.

The isolation by Payen and Persoz[1] of the enzyme diastase from the extract of barley malt was succeeded by the discovery of emulsin in bitter almonds by Liebig, and the formulation of a theory of its mode of action, which, however, in view of the preceding review of Faraday's work, is wrongly stated by Ostwald[2] to be the first theory of catalytic action.

In propounding a theory of catalytic action Liebig was animated with the purpose of demonstrating that the Berzelian concept of a special catalytic force was superfluous. As originally expressed, the cause of catalytic action lay in the facility possessed by a body in decomposition or combination of communicating to another body in contact with it the same chemical activity or the same powers of combination which the body itself possessed. In illustration of this property, Liebig cited the combustion of a body by bringing it into contact with a body which is itself undergoing combustion, and, in further illustration, the solubility of platinum when alloyed with silver in acids in which normally the platinum alone remains insoluble.

The illustrations chosen by Liebig can scarcely be described as happy, since, as Berzelius very readily pointed out,[3] numerous researches had already shown that a burning body was not necessary for the production of combustion. Even cold platinum sponge was sufficient to bring about the ignition and also explosive combustion of hydrogen and oxygen. On the other hand, the solubility of platinum when alloyed with silver was not to be explained on Liebig's assumptions, since, as Berzelius emphasised, solution of platinum was not effected when present in alloys with iron, copper, zinc, or mercury.

Liebig was therefore constrained to modify his theory of catalytic action, and did so in reference to the problem of sugar fermentation. The hypothesis became one of "molecular vibrations", communicable, by contact, to another body, thus setting up in the atoms of the second system similar motions leading to reactions or decomposition. In the particular case of sugar fermentation, this would involve that the decomposing yeast-cells, in the process of decomposition, induce instability in the molecules of sugar which thereby suffer accelerated decomposition to alcohol and carbon dioxide.

The disadvantage of the Liebig theory lies in its unassailability, since no possible test of the theory can readily be devised. It is comprehensive, and as such has earned considerable popularity, owing to its applicability to numbers of imperfectly understood reactions; but, as Ostwald pointed out,[1] it is of but little use as an auxiliary to scientific research, for the direction and suggestion of new lines of investigation. The theory called forth the following caution from Berzelius: In science, one always loses by plausible explanations published prematurely; the only correct method of attaining certain knowledge is to be found in leaving the incomprehensible until the explanation sooner or later is given by facts which are so clear that divided opinion upon the matter can scarcely arise. The procedure thus recommended by Berzelius was faithfully exemplified in the researches of Schonbein, to whom is due many of the facts of the problem of catalysis which we at present know, but who partook to no extent in the theoretical discussions as to cause

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[1] *Ann. Chim. Phys.*, 1833 (ii.), 53, 73.

[2] "Über Catalyse", *Vers. Ges. Deutsch. Naturforscher und Ärzte*, Hamburg, 1901.

[3] *Jahresber.*, 1841, 20, 452.

The action of oxides of nitrogen in the lead chamber process possesses considerable historical interest in regard to catalysis, since the explanation originally put forward by Clément and Désormes[2] involving a series of cyclic reactions, the alternate formation and decomposition of "chamber crystals", may be regarded as the first attempt to explain a catalytic process by what has come to be termed the intermediate compound theory In all the early discussions of the nature of catalytic processes this case was apparently overlooked The corresponding explanation of the etherification process by Williamson in 1854,[3] involving the intermediate formation and subsequent decomposition of ethyl sulphuric acid, established the concept of intermediate compound formation and led eventually to its extended application to the theoretical interpretation of catalytic processes in which the stoichiometric relationships were not so definitely established.

In the development of a subject so intimately concerned as is catalysis with the conception of velocity of reaction the researches of Wilhelmy,[4] entitled "On the Law according to which the Action of Acids on Cane-sugar Occurs", call for special reference The importance of the researches lies in the fact that they were the first successful attempts to study the operation of the time factor in chemical reaction Wilhelmy showed with reference to the hydrolysis of cane-sugar that the rate of inversion was at any moment proportional to the amount of cane-sugar undergoing transformation, in strict agreement with the mathematical equations which he developed from general considerations. The research, moreover, is the first successful attempt to establish the law of mass action in a quantitative manner. Wilhelmy further studied the influence of temperature and concentration of acid in reference to reaction velocity, without, however, coming to any important conclusions At the close of his research Wilhelmy remarks: "I must leave it to the chemists to decide, whether and how far the formulæ obtained are applicable to other chemical processes; in any case, all those processes to which one ascribes the operation of a catalytic force seem to me to belong to this class." As Ostwald has pointed out, the research was overlooked by numerous later investigators, and it was not until the attention of men of science had been directed to the work by Ostwald[1] that it was recognised that Wilhelmy is to be designated the discoverer of the laws of chemical reaction velocity, since the formulæ which he put forward were subsequently shown to be applicable to a number of chemical processes. The extension of Wilhelmy's work was undertaken by Löwenthal and Lennsen,[2] who showed that the velocities with which the acids invert cane-sugar is proportional to the strengths of the acids. The influence of temperature on reaction velocity was successively studied by Berthelot,[3] by Harcourt and Esson,[4] and later still by Warder,[5] Urech,[6] van 't Hoff, Arrhenius, and many others.

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[1] *Loc. cit.*

[2] *Ann. Chim.*, 1806, 59, 329

[3] *Ann. Chim. Phys.*, 1854 (iii.), 40.

[4] *Pogg Ann.*, 1850, 81, 413, 499.

Ostwald claims to have introduced the concept of reaction velocity as a definite criterion of a catalytic process by his insistence, since 1888, on the point of view that the catalyst is to be regarded as accelerator (or inhibitor) of a reaction already taking place, in contradistinction to the concept that a catalyst can initiate a reaction. In agreement with this idea, the following definition of catalysis was put forward by Ostwald: "Catalysts are substances which change the velocity of a given chemical reaction without modification of the energy factors of the reaction."[7] It is claimed by Ostwald for this change, slight though it appears, that it has yielded important results in the scientific development of the subject, since it has facilitated exact investigation of the magnitude and character of such acceleration. The point of view thus put forward does not enjoy universal acceptance. Schönbein, J. J. Thomson, H. E. Armstrong, and Duhem have all indicated their opinion that a catalyst may actually initiate a reaction.

Of the early efforts in the study of catalysis there remain for consideration those which have reference to the influence of the catalyst on reversible processes. As early examples among these may be cited the researches of Lemoine[8] on the decomposition of hydriodic acid, as a type of a heterogeneous catalysis, and those of Berthelot[9] on the equilibria attained in esterification processes, as a type of homogeneous catalysis.

Lemoine demonstrated that in presence of platinum sponge the decomposition limit at 350° was 19 per cent, attained practically immediately. On the contrary, operating without a catalyst at the same temperature under a pressure of two atmospheres, a limit of

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[1] *J. pr. Chem.*, 1884, 29, 385.

[2] *Ibid.*, 1862 (i.), 85, 321, 401.

[3] *Compt. rend.*, 1864, 59, 616 *et seq.*; *Ann. Chim. Phys.*, 1869 (iv.), 18, 146.

[4] *Phil. Trans.*, 1867, 167, 117.

[5] *Amer. Chem. J.*, 1881, 3, 203.

[6] *Ber.*, 1883, 16, 762; 1884, 17, 2165; 1887, 20, 1836.

[7] *Chemische Betrachtungen*, "Die Aula", 1895, No. 1.

[8] *Ann. Chim. Phys.*, 1877 (v.), 12, 145.

[9] *Bull. Soc. Chim.*, 1879, 31, 342.

18·6 per cent decomposition was attained, although only after an interval of 250 to 300 hours.

Berthelot established the same independence of the equilibrium state in the esterification of alcohols by acetic acid, in the absence, and in presence, of traces of mineral acid catalysts such as hydrochloric or sulphuric acid. At the ordinary temperature the equilibrium state was reached with equivalent initial concentrations of alcohol and acid when 66 per cent of the alcohol had been converted in either case, the time required, however, involving years of contact in the absence of catalyst as opposed to a few hours in presence of the mineral acid. In the subsequent theoretical discussion it will emerge that the rôle of the catalyst in the question of equilibrium has a very considerable significance, and has therefore been the object of numerous investigations. The manifold directions which these have assumed necessitate special and individual treatment not consonant with an historical survey, and consequently further discussion will not be intruded at this juncture

From 1880 onwards the studies of catalytic reactions rapidly multiplied They were concerned with all the many-sided aspects of the problem On one hand, investigations yielded advance in the knowledge of theoretical principles underlying catalytic change. On the other, carefully conducted investigations added to the list of reactions capable of catalytic acceleration, a list which, judging by the investigations of Thénard [1] on hydrogen peroxide decomposition, or by the speculations of Ostwald, might well become comprehensive of all chemical reactions Catalytic processes were employed with signal success in the studies inaugurated by the theory of electrolytic dissociation of Arrhenius and in the development of modern physical chemistry which resulted from that theory and the theory of dilute solutions of van 't Hoff At the same time there was developing, constantly and consciously, the application of catalysis to industrial enterprise, which has yielded results the importance of which can be adjudged from a consideration of the manufacture of synthetic indigo, of contact sulphuric acid, of synthetic ammonia, or of the modern hydrogenation of fats.

It is to the many features of all such developments that attention will, in the succeeding chapters, be directed

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[1] *Ann. Chim. Phys*, 1818, 9, 314.

CHAPTER II

CRITERIA OF CATALYSIS

In the preceding chapter relative to the early history of catalysis it has been shown that a large number of reactions proceed in the presence of suitable agents, which, following the nomenclature of Berzelius, are called catalytic agents, the reactions themselves being spoken of as examples of catalysis. Thus far, however, no exact definition of catalytic action has been laid down, and little has been said as to criteria of catalysis beyond the definition attributed to Ostwald, in which the acceleration of a reaction by the presence of a given substance is regarded as a criterion of catalytic action. In order, therefore, to delimit the field of chemical science with which this survey is concerned, it is necessary to proceed to an examination of the various tests which may be applied to a given chemical operation in order to ascertain whether, in the process thereof, the phenomenon of catalysis intrudes. The criteria thus laid down it will be advantageous to illustrate by reference to typical examples and to the research work which has been conducted with a view to verification.

The fundamental characteristic of all catalysed processes is that they are reactions which, in the thermodynamic sense, are classed as spontaneously occurring processes. That is, they are reactions which occur with diminution of free energy. Any such reaction which is accelerated by the presence of an added substance may be classed as a catalytic action, and the agent added may be regarded as the catalyst or catalytic agent. The catalyst therefore operates to produce equilibrium, in a system removed from the equilibrium state, more rapidly than this would be achieved in the absence of the catalyst. This characteristic limits fundamentally the range of catalytic study. Thus, while it encourages a search for catalysts which will promote the combination of nitrogen and hydrogen to the extent which modern physico-chemical studies have shown to be possible from the thermodynamic data in question, it discourages definitely a search for accelerating agents for reactions opposed to the normal free energy relationships of the reaction system. Search is useless for a catalytic agent which shall transform, for example, large quantities of oxygen, at room temperature, into ozone, since the equilibrium concentration of ozone in presence of oxygen, at room temperature, is vanishingly small. Similarly, it is not possible, with the aid of a catalytic agent, to achieve, at a given temperature, an equilibrium concentration of a resultant equal to that prevailing at some other temperature, if the equilibrium concentration varies markedly with temperature. More concretely, we may say that, in the production of nitric oxide from nitrogen and oxygen, it is not possible to achieve with the aid of a catalyst, at lower and more practicable temperatures, the equilibrium concentrations of the oxide which are normally obtained at the high temperature of the electric arc. For, such concentrations would be greater than the equilibrium concentrations at the lower temperature concerned, since the combination of nitrogen and oxygen to form nitric oxide is endothermic, and the catalyst would be therefore employed in achieving a reaction in opposition to the normal free energy of the process It should be demonstrable, in all the numerous types and examples of catalytic processes discussed in the following pages, that they are reactions involving a diminution of free energy, reactions progressing towards the normal equilibrium condition of the system

The criterion of velocity increase is an essentially practical criterion, for on this is based a differentiation in catalytic efficiency From the practical standpoint, the addition, to a reaction system, of a substance which has no influence either on the equilibrium or on the speed with which equilibrium is attained is without interest, although from the theoretical standpoint interesting problems might be involved Catalytic efficiency will be judged either by the relative accelerations produced by equal quantities of added catalytic agents or by the relative concentrations of added agents which are required to produce a given acceleration The mechanism by which the acceleration is produced in the two cases may be entirely different Furthermore, relative efficiencies may vary with variation in the physical conditions under which the reaction is carried out These two factors may be illustrated conveniently by the so-called water-gas reaction,

$$CO + H_2O = CO_2 + H_2,$$

with two catalytic agents copper and oxide of iron Over the range 200°-300° C copper is more efficient than iron oxide as a catalyst for this reaction.[1] Above 300° C, however, iron oxide is quite definitely the more efficient, and, in the region of 400°-450° C, equilibrium conversions are readily achieved. With copper, at these temperatures, a relatively low and decreasing efficiency is found. Armstrong and Hilditch show that this varying efficiency and order of efficiency may be attributed to the differing mechanisms whereby the reaction in question is achieved. Whereas, in the case of copper, the products appear to be formed via formic acid as an intermediate stage, in the presence of iron oxide an alternate reduction of the oxide by carbon monoxide and oxidation of the reduction product by steam apparently occur. It is evident from this, also, that mechanism cannot be involved in the criteria of catalysis.

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[1] Armstrong and Hilditch, *Proc. Roy. Soc.*, 1920, 97A, 265.

Certain additional observations of facts in regard to catalytic processes may now be made. The catalytic agent is present in the reaction system on completion of the reaction process. If, therefore, the reaction products be removed and further quantities of the reactants be brought into contact with the catalyst, the process can be repeated and the sequence thereby continued indefinitely. Herein lies one of the principal practical advantages of the catalytic agent, since it ensures that, with minimal amounts of catalyst, large quantities of the reacting substances may be transformed. So long ago as 1806, observation of the cyclic nature of the reaction of oxides of nitrogen in the lead chamber process of sulphuric acid manufacture led Clément and Désormes to this conclusion, which is universally valid in all cases in which the possibility of secondary reactions is excluded. These latter, however, are by no means infrequent, and so it is common in the literature of catalytic agencies to refer to the "life" of a catalyst. This may be stated in a variety of ways, all of which, however, are referable to the ratio of reactants transformed to catalytic material employed.

In illustration of the several points thus raised in connection with the quantity of catalyst required for the transformation of reacting substances, the following examples may be cited. Bredig has pointed out that the combination of hydrogen and oxygen at the ordinary temperature could be brought about by 2·5 c.c. of a colloidal solution of platinum containing as little as 0·17 milligram of platinum, and that, at the outset, the rate of combination was 1·8 c.c. of gas per minute. After a period of time during which 10 litres of gas had undergone combination, it was found that the activity of the colloidal solution was still unimpaired, the velocity of combination being, within the experimental error, identical with that prevailing at the commencement. Mellor[1] cites the observation of Titoff[2] that the presence of 0·0000000000001 N. $CuSO_4$ solution is sufficient to produce a perceptible acceleration of the rate of oxidation of an aqueous solution of sodium sulphite.

Sulphuric acid is the usual catalyst for the dehydration of alcohol to yield ether. As operated in modern technical practice, secondary reactions are practically excluded, so that an initial quantity of sulphuric acid is sufficient for the transformation of large quantities of alcohol. In the laboratory, and also in less modern types of technical plant where the control of the process is by no means so certain, it is a matter of common observation that, in addition to the etherification process, side reactions intrude, manifested by charring of the organic material and reduction of the sulphuric acid to sulphur dioxide. In such circumstances the catalyst shows a steadily diminishing efficiency, so that, sooner or later, replacement of the acid becomes necessary. Such an example illustrates the importance of the problem of side-reactions to the main catalytic process in the technical application of catalysis. It will emerge later in the discussion on "catalyst poisons" that in such cases as the contact sulphuric acid process, the synthesis of ammonia and its oxidation to nitric acid, as well as in many other reactions of technical importance, the essentials of success are to a considerable degree governed by the elimination of materials which, by reaction with, or modification of, the catalytic material, suppress practically entirely the activity of the catalyst Such side-reactions eliminated, however, technical catalysts are oftentimes very long lived. Examples are known of contact masses in sulphuric acid manufacture in which the platinum catalyst has remained efficient during a period of ten years of manufacture, being finally discarded rather by reason of high resistance to the passage of the gases than for loss of catalytic activity

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[1] *Chemical Statics and Dynamics.*

[2] *Zeitsch. physikal. Chem.*, 1903, **46**, 641.

In heterogeneous catalytic reactions the physical condition of the catalyst may be modified as a result of its participation in the reaction process. In many cases, such change in physical condition is a necessary preliminary to the attainment of full efficiency. Dobereiner's platinum wire becomes covered, after reaction, with a finely divided deposit of metallic platinum, or corroded or pitted in the process of catalysing the hydrogen-oxygen combination The same phenomenon is observed in the case of the platinum wire forming the gauze used as catalyst in the modern technical process for the oxidation of ammonia with air or oxygen, and Bone has illustrated its occurrence in the employment of silver gauzes in surface combustion processes

The change in physical state of the catalyst is generally attributed to its activity in a series of cyclic actions in which the material participates, the final reaction of the cycle resulting, however, in the regeneration of the catalytic material in its initial form Thus, in the well-known action of manganese dioxide in promoting the decomposition of potassium chlorate with evolution of oxygen, it has been observed that if initially a crystalline form of the oxide be employed, the final product is manganese dioxide in the form of a fine powder. The researches of Sodeau [1] have associated this change in physical state with the participation by the manganese oxide in the process of chlorate decomposition. Langmuir [2] compares the changes that occur in the surfaces of metals used as catalysts with the "offsetting" of tantalum filaments, or improperly made tungsten filaments, when run in lamps on alternating current The offsetting consists of a slipping of the crystals of the metals along the boundary planes, and, in extreme cases,

hem. Soc., 1900, 77, 137, 717; 1901, 79, 247, 939; 1902, 81, 1066.

[2] *Trans. Farad. Soc.*, 1922, 17, 618.

it leads to a disintegration of the structure of the metal. The effect has been shown to be dependent upon the rapidity of temperature fluctuation. The same is true of the surface of the target in an X-ray tube run on alternating current. Introduction of gases intensifies the effect. Langmuir concludes that, in all these cases, the disintegration is to be ascribed to sudden fluctuations in temperature between adjacent atoms in the metal.

Catalysts and equilibrium.—We may now turn our attention to the question of equilibrium in catalysed reactions. It will be useful to consider the problem fundamentally, in reference to a perfectly general reaction. Let us assume a reaction between a moles A and b moles of B to yield c moles of C and d moles of D. Let a concentration of x moles of the catalyst X be present throughout the reaction process. We may express this process by the equation

$$aA + bB + xX = cC + dD + xX.$$

For a dilute gaseous system, obeying the gas laws, it may readily be shown, either kinetically or thermodynamically, that, at equilibrium,

$$K_p = \frac{P_C^c \times P_D^d \times P_X^x}{P_A^a \times P_B^b \times P_X^x} = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}, \qquad (1)$$

where P refers to the partial pressure of the given species at equilibrium. It can readily be seen that the right-hand member of Expression (1) is identical with the equilibrium expression for the non-catalysed reaction, which signifies that the value of K_p is identical for both catalysed and non-catalysed reactions in a dilute gaseous system.

Similarly, for the same reaction occurring in an ideal solution, it can also be shown that, at equilibrium,

$$K_M = \frac{M_C^c \times M_D^d \times M_X^x}{M_A^a \times M_B^b \times M_X^x} = \frac{M_C^c \times M_D^d}{M_A^a \times M_B^b}, \qquad (2)$$

where M refers to the mol fractions of the several species at equilibrium. Correspondingly, for a very dilute solution in which the laws of dilute solution hold, we obtain

$$K_C = \frac{C_C^c \times C_D^d \times C_X^x}{C_A^a \times C_B^b \times C_X^x} = \frac{C_C^c \times C_D^d}{C_A^a \times C_B^b}, \qquad (3)$$

where C refers to the molecular concentrations of the several species at equilibrium. In these cases, also, it is manifest that the equilibrium constants remain unchanged in the catalysed process or that the catalyst does not alter the position of equilibrium in systems composed of ideal or very dilute solutions.

Actual reaction systems deviate to a greater or less degree from the ideal systems which we have just discussed. For this reason, it has become general in recent years, in discussing problems of chemical equilibrium, to employ the concept of the activity of a reaction species in place of one or other or all of the concepts possible with ideal systems.[1] The activity of a species may be defined essentially by the equation

$$F_A = RT \ln a_A + C_A, \qquad (4)$$

where F_A is the molal free energy of the substance A under given conditions, a_A is its activity, and C_A is a constant which may be arbitrarily defined. The increase in free energy when a substance changes from one set of conditions to another is given from Equation (4) by the expression

$$F_{A'} - F_A = \Delta F_A = RT \ln \frac{a_{A'}}{a_A}, \qquad (5)$$

where a_A and $a_{A'}$ represent the activities in the initial and final stages respectively and ΔF_A represents the increase in free energy accompanying the change. The essential criterion of a condition of equilibrium in any system at constant temperature is that the free energy change accompanying any process occurring shall be zero. For the reaction,

$$aA + bB = cC + dD,$$

at the condition of equilibrium,

$$aF_A + bF_B = cF_C + dF_D \qquad (6)$$

By combining Equations (4) and (6) we therefore obtain

$$aRT \ln a_A + aC_A + bRT \ln a_B + bC_B$$
$$= cRT \ln a_C + cC_C + dRT \ln a_D + dC_D \qquad (7)$$

or

$$aC_A + bC_B - cC_C - dC_D = RT \ln \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}, \qquad (8)$$

or, since by definition the quantities on the left-hand side are constant, we may write for any given temperature

$$K_a = \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b},$$

where K_a may be termed the equilibrium constant in terms of the activities of the reacting constituents. This equation is independent of any simplifying assumptions and may be regarded as perfectly general for any chemical reaction.

Now this equation has been derived from considerations of the initial and final states of the system independently of any mechanism whereby the process is achieved. Hence it follows that the activity constant Ka and the free energy change for the reaction, must be unaffected by the presence of any substance occurring on both sides of the equation, provided the equation is otherwise unchanged. This will be true for a gaseous mixture passing over a solid catalyst which is unchanged on completion of the reaction process. The equilibrium partial pressures of the gases issuing from the reaction zone will be identical with those which would be yielded at equilibrium from the same gas mixture in absence of a catalyst. In all cases of this type it is clear that the catalyst cannot affect the equilibrium in the gas phase. *No case is known in which a change in equilibrium has been experimentally demonstrated in reactions of this type.*

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[1] For a general treatment of the concept of activity, see Taylor, *Treatise on Physical Chemistry*, chapters viii and xii (D. Van Nostrand & Co., New York, 1924; Macmillan & Co., London, 1925), or Lewis and Randall, *Thermodynamics and Chemistry* (McGraw-Hill Co., 1923).

In homogeneous systems involving a catalyst it is, however, possible that the equilibrium concentrations of a reaction system may be modified by the presence of a catalyst. It is possible to indicate how this occurs. If the activity of the catalytic agent remains unchanged throughout the reaction, the derivation of Equation (9) indicates that the equilibrium constant K_a remains unchanged in presence of the catalyst. The catalyst, however, may have widely varying effects on the activities of the several reactants; in such case, the mol fractions or the molecular concentrations of these several reactants may have appreciably different values from those obtaining in the absence of a catalyst. It is to this varying effect of a catalytic agent on the activities of the individual reacting species that most of the abnormalities in the determination of equilibria in the presence of catalysts are to be attributed. The effect is particularly apt to occur in equilibria which involve electrolytes either as reactants or as catalysts.

Equilibrium determinations in processes of ester hydrolysis may be cited in illustration of this factor. Jones and Lapworth[1] investigated the equilibrium constant in the hydrolysis of ethyl acetate, using hydrochloric acid as catalyst. It was found that the value obtained for the equilibrium constant in terms of concentrations of the reacting species varied according to the amount of catalyst employed. The appended diagram (Fig. 1) gives a plot of the values of the apparent equilibrium

$$\Psi = \frac{[H_2O][CH_3COOC_2H_5]}{[C_2H_5OH][CH_3COOH]},$$

where the brackets indicate mol fractions. It will thus be seen that the value of $\Psi(=4)$ obtained by Berthelot and Paen de St. Gilles for such homogeneous liquid systems in presence of traces of acid catalyst, rises steadily with increasing concentrations of hydrochloric acid to values in the neighbourhood of 9. This is to be ascribed to the influence of the acid on the activity of the water, and, probably to a lesser extent, the other constituents. The activities of these constituents are then no longer proportional to their mol fractions. Rising values are obtained for Ψ. If the equilibrium constant Ka were calculated from the several activities in presence of varying concentrations of catalyst, a real constancy would be observed. Similar measurements by Armstrong and Worley[1] also show the dependence of the end-point in acid hydrolysis of esters on the concentration of acid catalyst employed The variations observed are determined by the influence of the acid on the activities of the several reacting species. The introduction of the concept of activity into the mathematical treatment of reaction velocity has been given most comprehensively by Bronsted.[2] Details of this will be given in a later chapter on the kinetics of homogeneous catalytic actions Bjerrum[3] has pointed out that Bronsted's equation, involving activities of the several molecular species, really involves the concentration of a reacting complex formed by collision of these reacting species

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[1] *J. Chem. Soc.*, 1911, **99**, 1427.

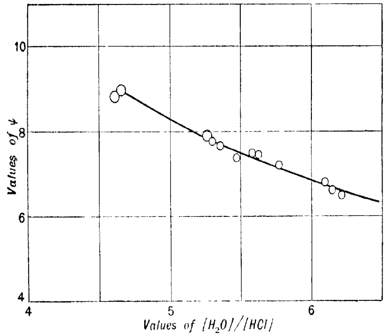

FIG 1

The more closely a reaction system approximates to that of an ideal system, whether gaseous or in solution, the more nearly independent of either the catalyst employed or the concentration of catalyst does the equilibrium become As the condition of ideality is approached, the more closely proportional are activity and concentration. That this is approximately realised in some circumstances is evident from the researches of Koelichen[4] on the reversible transformation of acetone to diacetonyl alcohol

$$2CH_3COCH_3 = CH_3COCH_2 \ C(CH_3)_2OH$$

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[1] *Proc Roy Soc*, 1912, **87** A, 604

[2] See especially *Zeitsch physikal Chem*, 1922, **102** 169

[3] *Zeitsch. physikal Chem*, 1923, **108**, 82

[4] *Zeitsch physikal. Chem*, 1900, **33**, 129.

The reaction is catalytically accelerated by hydroxyl ions. The same equilibrium state is attained from either side by such varied agents as ammonia, triethylamine, tetraethyl ammonium hydroxide, and sodium hydrate. Turbaba,[1] also, varied the catalytic agent in the aldehyde-paraldehyde equilibrium, showing that with hydrochloric acid, sulphur dioxide, oxalic acid, zinc sulphate, and other agents the proportion transformed was independent of the nature and quality of the catalytic agent.

There are few direct experimental demonstrations that, in gaseous reactions at a solid surface, the equilibrium position is unchanged. Lemoine's data on hydrogen iodide decomposition at a platinum surface and in absence of such have already been cited in the preceding chapter. Of indirect evidence, however, the literature is full. Every case in which a shift of equilibrium has been suspected has been shown, on closer examination, to be quite normal Thus, Jellinek[2] suspected that ammonia in excess of the normal equilibrium concentrations might be obtained from nitrogen-hydrogen mixtures in presence of catalytic iron. A most careful study by Larsen[3] has failed to reveal any indication of this whatever. It was suspected by some that the experiments of Milligan, Chappell, and Reid[4] on esterification of alcohol-acetic acid vapours in presence of silica gel indicated a shift of the esterification equilibria, since yields considerably in excess of 66 per cent ester were obtained. This suspicion was unfounded. It arose from a confusion of the equilibrium state in liquid system with that in the vapour phase. Berthelot and Paen de St. Gilles had shown that, in liquid system, the equilibrium position lay in the neighbourhood of 66 per cent ester formation from equimolecular quantities of alcohol and acetic acid. But, as was recently shown by Edgar and Schuyler,[5] in the vapour phase, the equilibrium point is much more markedly on the ester side.

There exists, however, a wealth of indirect evidence that the solid catalyst does not shift the equilibrium in a gaseous reaction. The concordance which exists between the thermodynamic calculations of equilibrium in a variety of gas reactions and the direct experimental measurements of the equilibrium, most of which have been achieved with the aid of catalytic agents, is at once a convincing proof that equilibrium is independent of the catalyst. Thus, for example, the equilibrium in the Deacon chlorine process as determined by Lewis[6] and by von Falkenstein[7] with the aid of catalytic agents, may be harmonised completely with the thermodynamic data for the process. Or, alternatively, the values obtained for the equilibrium in this reaction may be utilised to evaluate free energy functions of the reacting species, which data may in their turn be used for other calcula-

[1] *Zeitsch. physikal. Chem.*, 1901, **38**, 505.
[2] *Zeitsch. anorg. Chem.*, 1911, **71**, 121.
[3] *J. Amer. Chem. Soc.*, 1923, **45**, 2918; 1924, **46**, 367.
[4] *J. Physical Chem.*, 1924, **28**, 872.
[5] *J. Amer. Chem. Soc.*, 1924, **46**, 64.
[6] *J. Amer. Chem. Soc.*, 1906, **28**, 1380.
[7] *Zeitsch. physikal. Chem.*, 1907, **59**, 133.

tions, all of which by a system of check and cross-check can be shown to be in complete agreement. It is in this manner that the most decisive conclusion as to independence of equilibrium and catalyst in such gaseous systems can be achieved. The number of such examples is steadily increasing in the thermodynamic literature

There follows from this discussion of the catalyst and equilibrium the very practical conclusion that, in a reversible process, the catalyst must accelerate both the forward and backward reactions In such systems as show no shift of equilibrium with catalyst employed, the same proportionate acceleration will be produced in the inverse reactions. A hydrogenation catalyst will also be efficient in the reverse, dehydrogenation. An esterification catalyst will operate also as an agent for hydrolysis of the ester Numerous examples of this feature will be found in the subsequent chapters

Solvents and catalysis.—What has been said in the preceding section with respect to the influence of the catalyst on the activities of the several reacting species, and therefore upon the position of equilibrium, can be applied also to the influence of the so-called "indifferent" constituents of the reaction system Among these "indifferent" constituents the solvent is of first importance So long as the system is ideal the solvent will be without influence on equilibrium But, in so much as the solvent or any "indifferent" constituent exercises an influence on the activities of the reacting species, by just so much will its influence on the position of equilibrium be felt. There may exist a whole series of systems in which an added agent will vary at the one extreme from a catalyst, normally so called, to the other extreme in which it is commonly regarded as a solvent, and there will be nothing in principle to distinguish the catalyst in the one solution from the solvent in the other Thus, a little ether may act in benzene solution as a catalyst for the reactions of the Grignard reagent[1] By increasing the concentration of the ether continuously, a state of affairs may be obtained in which the ether may justly be regarded as the solvent In principle or mechanism nothing has been changed. Only in its quantitative aspects has the system undergone change In each case, reaction will be measured by the activities of the several molecular species

Since the activity of a substance in solution can only attain certain limiting values dependent largely on the solubility of the species in the given solvent, it is apparent that, from this cause, a solvent may exercise a directive influence on the course of reaction Thus, in aqueous solution, potassium iodide precipitates mercuric iodide from a solution of mercuric chloride In acetone solution, on the contrary, mercuric iodide is quite soluble, while potassium chloride is insoluble; hence, addition of mercuric chloride precipitates potassium chloride from acetone solutions of potassium iodide.

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[1] Tschelinzeff, *Ber.*, 1905, 38, 3664.

The problem of the solvent in the reaction process may also be examined from the standpoint of the solvation of the reacting species. If a reactant, A, undergoing change, forms, in a solvent S, a solvated molecule, the equilibrium condition being represented by the equation

$$A + nS = A \,.\, nS,$$

the solvent may exercise a profound influence on the rate of change. If unsolvated A alone undergoes reaction, then presence of the solvent S will lower the specific rate of reaction. If the solvated molecules, $A \,.\, nS$, are reactive constituents, several possibilities may arise. The observed reaction rate will depend on the value of n, which will influence the reactivity of the solvated reactant. The rate may also vary with the nature of the solvent S, and, whether due to the reactivity of either A or $A \,.\, nS$, the rate will also depend on the value of the equilibrium constant in the above solvation equilibrium.

Bjerrum has discussed some of these factors in a recent paper.[1] He points out that the enhanced catalytic activity of hydrogen ions in presence of neutral salts, first noted by Arrhenius, can be explained on the basis of varying hydration of the ion. If the ion in the intermediate complex formed by collision of the reacting species and the hydrogen ion have a smaller water content than the ion in the solution, the Arrhenius effect must result. Bjerrum points out that, if the difference in the two amounts to n moles of water, then the catalytic activity will increase, with decreasing vapour pressure of the solution p, to an extent proportional to $(p_0/p)^n$, where p_0 is the vapour pressure of pure water.

Bjerrum further points out that, besides these catalytic effects which may be associated with the formation of definite chemical compounds, and in which the catalyst, so to say, opens up a number of parallel reaction paths, there are certainly cases where the presence of materials foreign to the actual reaction process may actually exert an influence on the reaction speed without actually entering into combination with the reactants. These act by virtue of the molecular forces which they exert on the reacting complex, changing its form without the production of a chemical compound. A deformation of the reaction complex may occur which may have marked influence on the velocity of rearrangement of the complex. There is some evidence that such deformation catalysts are present in some catalytic gas reactions. Bjerrum points out that the relationship between deformation and activity will be slight. The activity of a substance at the same concentration is known to be greater in poor solvents than in good solvents. But it cannot thereby be concluded that the substance will react more rapidly in the poor solvent. Rather should one conclude that the reaction will proceed more rapidly in the good solvent, because, in this case, the greater solubility is an index of greater molecular forces which may influence the velocity of change by deformation.

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[1] *Zeitsch. physikal. Chem.*, 1923, **108**, 82.

Menschutkin[1] attempted to trace a relationship between the dielectric constant of the solvent medium and the velocity of interaction of triethylamine and the ethyl halides in various solvents. Some of his results are recorded in the following table

Solvent	Velocity Constant	Dielectric Constant
Hexane	0·00018	2·6
Xylene	0·00287	2·6
Benzene	0·00584	2·6
Ethyl alcohol	0·0366	21·7
Methyl alcohol	0·0516	32·5
Acetone	0·0608	21·8
Benzyl alcohol	0·1330	10·0

It is evident from this table that this physical property alone is inadequate to explain the whole of the variation in velocity

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[1] *Ber.*, 1882, **15**, 1818; *Zeitsch. physikal. Chem.*, 1887, **1**, 611; 1890, **5**, 589; 1890, **6**, 41

CHAPTER III

HOMOGENEOUS REACTIONS

Gas reactions.—The problem of the mechanism of homogeneous gas reactions is in reality not so simple as would be imagined from a direct interpretation of the "order" of the reaction.

There are, for example, numerous examples of reactions which are apparently unimolecular in character, and it was, as we shall have occasion to observe, on the hypothesis that a unimolecular constant for the reaction velocity was a true criterion of a unimolecular reaction that led Perrin to his formulation of the radiation hypothesis of chemical action. Apart from the radioactive transformations, however, very few true unimolecular reactions exist. The decomposition of phosphine examined by Trautz and Bhandarkar,[1] which at one time was taken as the classical example of a unimolecular reaction, has been shown by Hinshelwood[2] to be a heterogeneous reaction. On the other hand, the decomposition of nitrogen pentoxide investigated by Daniels and Johnston[3] has recently been shown by Hirst and Rideal to depart from the unimolecular law at pressures below 0·25 mm., but become unimolecular again at very low pressures. An interesting field for investigation would be the dissociation of such compounds as nitrogen tetroxide, of the diatomic molecules of the halogens, and the thermal ionisation of vapours, from the point of view of the order of the reaction. Whilst the pseudo unimolecular character of a number of decompositions or dissociations evidently requires explanation, the rarity of true unimolecular reactions is significant.

In the case of bimolecular reactions two points of great interest emerge from observations on the reaction velocities at various temperatures. It is found that the number of molecules reacting per c.c. per second falls far short of the number of actual collisions effected between the molecules of the reacting species. From this observation the division of collisions into "effective", where reaction results, and "ineffective", or those undergoing ideal elastic collision, may be made. Again, as pointed out by Arrhenius, the influence of temperature on bimolecular reactions is most marked. It is found that the temperature coefficients of chemical reactions are always relatively high, the velocity increasing exponentially with the temperature. The number of collisions per c c per second, according to the kinetic theory of gases, is given by the equation

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[1] *Zeitsch. anorg. Chem.*, 1919, **106**, 95.

[2] *J. Chem. Soc.*, 1924, **125**, 393.

[3] *J. Amer. Chem. Soc.*, 1921, **43**, 53.

$$N_0 = 2N_1N_2\sigma_1\sigma_2\sqrt{2\pi RT\left(\frac{1}{m_1}+\frac{1}{m_2}\right)},$$

where N_1N_2, $\sigma_1\sigma_2$, m_1, m_2 are the numbers, molecular diameters, and masses of the reacting molecules, it is clear that the exponential increase in the number of effective collisions with the temperature is much greater than the comparatively small increase in the number of total collisions These results, and more especially considerations based upon the influence of temperature on processes of esterification and hydrolysis in solution, led Arrhenius[1] to the concept of "active" molecules.

According to Arrhenius we must postulate in a reacting species an equilibrium existing between active and inactive molecules

$$A \rightleftarrows A'$$

Active molecules on collision produce chemical reaction, inactive molecules ineffective or elastic collision The conversion of the inactive to the tautomeric active form requires the supply of energy, the energy of activation, or the critical energy increment, the magnitude of which, as we shall see, can be determined in certain cases from the temperature coefficient of the reaction

An adequate interpretation of the simple bimolecular reaction requires an analysis of the mechanism of activation and the source from which this energy required for activation is drawn There is, however, in addition, a third complicating factor to be considered in such reactions, which can best be exemplified as follows The heat of dissociation of hydrogen is *ca* 84,000 per grm -molecule, or 1·37 10^{-19} cal. per molecule When two hydrogen atoms approach one another even at very slow speeds to effect union to a molecule, the energy of dissociation has to be liberated before the hydrogen molecule can exist It is clear that, in the case of a "head on" collision, combination is impossible; for, if the atoms are moving towards one another with identical speeds, before formation of the molecule is possible, both the heat liberated in the reaction and the kinetic energy originally possessed by the atoms have to be dissipated in some way. Two methods of dissipation suggest themselves the energy may be dissipated in the form of radiation, or a simultaneous collision with a third molecule or atom may take place, and this third member may be shot off again with the excess energy in some form. As we shall have occasion to note, if radiation is emitted in such bimolecular reactions it is certainly not monochromatic in character; on the other hand, evidence for the removal of the excess energy by a third molecule or atom in the internal form—for example, in the combination of sodium and iodine by sodium atoms—is by no means scanty. It would appear by no means improbable that termolecular reactions, or at least two bimolecular reactions occurring in sequence in a short time interval, are in reality by far the most common.

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[1] *Zeitsch. physikal. Chem.*, 1889, 4, 22, 1899, 28, 317

Although, as we have seen, recombination of atoms can only occur either through the mechanism of a termolecular reaction, or, if bimolecular, through the emission of radiation, certain other types of true bimolecular reactions are possible. In the case of decomposition of complex molecules by bimolecular collision, if the decomposition be an endothermic process, the difficulty to which attention has been drawn does not arise, whilst if the decomposition be exothermic the products of reaction can evidently dissipate the energy in a kinetic manner.

Again, it is conceivable that the union of complex molecules to one another or to atoms may occur, such as the union of atomic oxygen, chlorine, or hydrogen, to their respective molecules, through the agency of true bimolecular reactions, for, although energy in excess of the critical amount required for decomposition has to be dissipated, a mechanism of dissipation is provided in the third atom in the complex molecule.

We have referred to the fact that in the union between atoms either radiation must be emitted or termolecular collisions must occur, the third body, either atom or molecule, serving as an energy dissipator. Since reaction does not occur without such collisions, we may consider this to be a simple case of true catalytic action. The researches of Bonhoeffer [1] on the combination of hydrogen atoms and of Bodenstein and Lütkemeyer [2] on the combination of bromine atoms, indicate that these reactions proceed very much more slowly than anticipated on the assumption of simple bimolecular collisions effecting combination. Only one in every thousand of such collisions is effective, and this may well be termolecular. Beutler and Polanyi,[3] however, have shown that reaction between sodium atoms and halogens and halides may occur with an efficiency of 1 collision in 100, and 10^4 times more rapidly than can be accounted for by triple collisions.

It is interesting to examine how far we can investigate the operation of such catalytic action. It is clear that if the catalyst dissipates the energy in a kinetic manner that recombination of atoms should take place very much more rapidly in the presence of an indifferent gas, for the number of termolecular collisions will be increased. In reversible reactions the augmentation of the velocity of association by the indifferent gas should be accompanied by the augmentation of

[1] *Zeitsch. physikal. Chem.*, 1924, 113, 199.

[2] *Ibid.*, 1924, 114, 208.

[3] *Naturwissenschaften*, 1925, 13, 711.

velocity of dissociation, for the equilibrium will be unaffected by its presence To take a concrete example, if the rate of union of chlorine atoms be facilitated by a neutral gas, the rate of dissociation of the chlorine molecules must likewise be affected, since the equilibrium conditions defined by

$$K_p = \frac{[\mathrm{Cl}]^2}{[\mathrm{Cl}_2]}$$

remain unaffected No crucial test of this hypothesis has been made

We may also consider that the catalytic function of the third atom or molecule is to dissipate the energy in an internal and not kinetic form, and it is only those substances which can acquire this internal energy which act as catalysts As an example may be cited the union of sodium and iodine atoms effected by the volatilisation of sodium iodide in a hot bunsen flame and cooling the products of dissociation. An examination of the spectrum reveals the presence of the sodium *D* lines but not those of the ionised iodine

The values of the heats of reaction of the various possible changes are given below

$$\begin{aligned}
&\mathrm{Na\ gas} + \mathrm{I\ gas} = \mathrm{Na\ I} + 112{,}000\\
&\mathrm{Na} + \mathrm{I}' = \mathrm{Na\ I} + 144{,}000\\
&\mathrm{Na\ gas} + {}^1\!/_2\mathrm{I}_{2\ \mathrm{gas}} = \mathrm{Na\ I} + 94{,}500\\
&\mathrm{Na} + (e) \rightarrow \mathrm{Na} + 48{,}500\\
&\mathrm{I}' = \mathrm{I} + (e) - 82{,}000\\
&\mathrm{I} = \mathrm{I} + (e) - 185{,}000
\end{aligned}$$

It is clear from the data presented that the energy dissipated in the union of sodium and iodine atoms will be sufficient to ionise sodium atoms but not iodine, thus the sodium may be regarded as a catalyst but not iodine for the union of sodium and iodine atoms by removing 48,500 out of 112,000 calories in the form of internal energy which is afterwards re-emitted as visible radiation

Whilst a number of supposedly homogeneous gas reactions have during the past few years been shown to be heterogeneous in that the reactions may occur entirely on (*e g* ethylene and the halogens) or commence at (hydrogen and chlorine) the walls of the containing vessel, it cannot be said that the operation of a homogeneous catalytic gas reaction has been studied in detail It is possible that the catalytic influence of small traces of water vapour examined by Baker in such reactions as the dissociation of ammonium chloride or the union of carbon monoxide and oxygen may prove to be true cases of homogeneous catalysis, yet, as we shall note, in the case of the hydrogen chlorine combination, it is possible that surface action intrudes Nevertheless, the study of uncatalysed homogeneous gas reactions reveals some of the most interesting peculiarities associated with chemical reactions

The energy of activation or excitation.—As we have noted, Arrhenius was led to the concept of active and inactive molecules in which the equilibrium between these two tautomeric forms of the same substance shifted in favour of the active form with rise in temperature. This concept was subsequently extended by Arrhenius to explain the mechanism of catalytic influence, the addition of the catalyst being presumed to bring about an increase in the concentration of the active form.

The alteration of the velocity coefficient with the temperature could be formulated in the expression

$$\frac{d \log K}{dT} = \frac{E}{RT^2},$$

E being the energy required to transform one gram-molecule from the inactive to the active state.

It will be noted that Arrhenius makes no assumption as to the source of the energy of activation but simply postulates the existence of these two tautomeric types as well as a dynamic or mass law equilibrium between them.

Marcelin[1] advanced the problem a stage further by deducing from the Maxwell-Boltzmann principle of the distribution of energy an expression similar to that of Arrhenius. On the assumption that the internal energy of the molecules varies in conformity with the laws of statistical mechanics, and that a molecule reacts when it has acquired internal energy E in excess of the normal,[2] he showed that the rate of variation of the velocity constant with the temperature would be expressed by the relationship

$$\frac{d \log K}{dT} = \frac{E_c}{RT^2}.$$

Marcelin's E_c, termed the critical energy increment, is thus identical with the energy of activation E postulated by Arrhenius.

The concept of Marcelin that it is the "internal energy" of a molecule which renders it active, is similar if not identical with the conception of the "excited" molecule of the physicist.

The probability that a molecule will react after it has gained internal energy E_c may increase with augmentation of this internal energy content; we shall then obtain, adopting again the hypothesis of a statistical distribution in internal energy,

$$\frac{d \log K}{dT} = \frac{E_c + RT}{RT^2},$$

since E_c is usually great compared to RT; to test this modification of the equation for the temperature coefficient of reaction velocity would require experimental data of a high order of accuracy.

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[1] *Compt. rend.*, 1914, 158, 161.

[2] G. N. Lewis and Smith (*J. Amer. Chem. Soc.*, 1925, 47, 1513) assume that E_c is the internal energy of a reactive molecule, not the excess above the average internal energy content; there is no justification, however, for this assumption.

Since the energy of excitation or activation is internal in character, we must inquire how this energy is acquired, a point on which neither Arrhenius nor Marcelin expressed any opinion.

Two methods have been suggested, one by the absorption of radiation, the other by means of molecular collision of a special type.

The radiation theory of activation.—In 1906 Trautz,[1] and independently both McC. Lewis [2] and Perrin,[3] suggested that the energy of excitation might be obtained from radiation normally existing and flowing through the reaction system

Perrin was led to this point of view by consideration of the mechanism of unimolecular actions. For such actions the probability of a particular isolated molecule decomposing within the next second is invariant, since the velocity constant is independent of the concentration The critical energy increment can evidently only be supplied by some non-material type of energy transfer such as radiation, either in the infra-red or other portion of the spectrum Trautz and Lewis were led to the same view by a supposed analogy between photochemical and thermochemical reactions. The extraordinary simplification which would be introduced into chemistry if chemical activation were always produced by the absorption of radiation is the great attraction of the radiation hypothesis

It was suggested by Trautz and McC Lewis that the activating radiation was monochromatic in character, and that its frequency could be determined from the energy of activation as defined by Arrhenius with the aid of the quantum hypothesis from the equation

$$E = Nh\nu,$$

where E is the energy of activation, h Planck's constant, and ν the frequency of the activating radiation

Since the activating frequency must be absorbed by the reacting system, it necessarily follows from this assumption that we can calculate at least one line in the absorption spectrum of a substance undergoing thermal decomposition from the temperature coefficient of that decomposition. It has to be admitted that the experimental proof of this hypothesis is inconclusive Whilst in some cases the theoretical anticipations have been verified, *e g.* for the decomposition of triethyl sulphine bromide dissolved in various solvents such as nitrobenzene, where van Halban [4] obtained a value of $E = 28{,}530$ cals. (λ cal. $= 1{\cdot}0\ \mu$), and McC. Lewis and H A Taylor [5] observed a strong absorption line at 1·05 μ. In the case of the decomposition of phosphine and nitrogen pentoxide the lines anticipated are not observed [6]

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[1] See also *Zeitsch. physikal Chem.*, 1911, **76**, 129, *Zeitsch anorg Chem.*, 1918, **102**, 81; 1919, **106**, 149

[2] *J Chem Soc*, 1916, **109**, 796.

[3] *Ann. Physik*, 1919, **11**, 5.

[4] *Zeitsch physikal Chem.*, 1909, **77**, 129.

[5] *J. Chem Soc.*, 1922, **121**, 665.

[6] Langmuir, *J Amer Chem. Soc.*, 19, **42**, 2190.

Even in those cases in which the anticipated line has been shown to exist, it still remains to be proved that irradiation with light of this frequency will promote photochemical decomposition.

Two other serious criticisms of this presentation of the radiation hypothesis may be advanced. As originally suggested by van t' Hoff and emphasised by Lindemann,[1] unless a light dart or corpuscular nature be attributed to radiation it is difficult to see why all the molecules should not absorb radiation equally and all disintegrate simultaneously; we should thus be confronted with a supposed homogeneous reaction proceeding almost explosively at the surface exposed to radiation. Again, Langmuir has pointed out the great discrepancy between the amount of radiation of the particular wave-length available in a supposed black body enclosure and the actual amount of decomposition effected by it. Langmuir[2] has utilised as his basis of argument the figures for the decomposition of phosphine given by Trautz and Bhandarkar, which are now known to be erroneous. Watson has performed a similar calculation for the decomposition of ethoxyoxalacetic ester, which decomposes according to the unimolecular law.

According to Planck the radiant energy in a black body enclosure encompassed within a band of thickness $\delta\lambda$ is

$$E_\lambda = \frac{2\pi^2 ch}{\lambda^5} \cdot \frac{1}{e^{ch/\lambda kT} - 1} d\lambda.$$

In the case of the decomposition of ethoxyoxalacetic ester the energy of activation as calculated from the temperature coefficient of the velocity constant was found to be 35,800 cals., and the absolute velocity constant to be $5{\cdot}37\ 10^{-4}$ at 183° C. Assuming a density of unity the energy required per c.c. per second is

$$\frac{35{,}800 \times 5{\cdot}37 \,.\, 10^{-4}}{232} \times 4{\cdot}2\ 10^7 \text{ ergs.} = 3{\cdot}10^6 \text{ ergs.}$$

The wave-length corresponding to the critical increment of 35,800 calories is, according to the Einstein equation, $E = Nh\nu$ and $\nu = \frac{c}{\lambda}$, $\lambda = 800\mu\mu$. Assuming a spectral width for this line of $10\mu\mu$, we obtain $E_\lambda = 2{\cdot}1\ 10^{-7}$ erg./sec. Thus one square centimetre of black body in contact with the ester would supply but an infinitesimal quantity of the actual energy required. This discrepancy between the observed reaction rate and the monochromatic radiation flow has been investigated by Christiansen,[3] and Christiansen and Kramers,[4] in which they show that the maximum rate of activation by radiation per c.c. per second is given by the Einstein expression

$$\frac{\partial N}{\partial t} = NB\rho\nu,$$

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[1] *Trans. Farad. Soc.*, 1922, **598**, 17.

[2] *Zeitsch. physikal. Chem.*, 1922, **103**, 91.

[3] *J. Amer. Chem. Soc.*, **42**, 2190.

[4] *Ibid.*, 1923, **104**, 459.

where N is the concentration of inactive molecules, $B.\rho\nu$ is th *probability per second that a molecule will become active under th influence of black body radiation of radiation density* $\rho\nu$ The rate of reaction is likewise proportional to the number of active molecules or

$$k = A\frac{P_a}{P_n}e^{-\frac{E}{RT}},$$

where P_a and P_n are the *à priori* probabilities of molecules existing in the active and normal states They find

$$NB\rho\nu = NA\frac{P_a}{P_n}e^{-\frac{E}{RT}}(1-e^{-E/RT}),$$

for large values of E this reduces to

$$NB\rho\nu = NA\frac{P_a}{P_n}e^{-\frac{E}{RT}},$$

and, if P_a/P_n be not very different from unity, the rate becomes

$$k = Ae^{-\frac{E}{RT}} = B\rho\nu,$$

where $\frac{1}{A}$ is the life of an excited molecule This is assessed as equal to 10^{-8} seconds

Tolman[1] has attempted to evaluate B from the Bohr correspondence principle by means of the expression

$$B = \frac{2\pi^3e^2}{3h^2}E^2,$$

leading to values of B from 10^{14} to 10^{19} Hence an upper limit is found for $k = 10^{20}\rho\nu$, and evaluating $\rho\nu = \frac{8\pi h\nu^3}{c^3}e^{E/RT}-1$ (or approximately $\frac{8\pi h\nu^3}{c^3}e^{-\frac{E}{RT}}$) we obtain $k = Ca\ 10^7e^{-\frac{E}{RT}}$ for $E = 25{,}000$ calories

Now the rate of a number of supposedly unimolecular reactions[2] is of the order of $10^{14}e^{-\frac{E}{RT}}$, whence a rate of $10^8e^{-\frac{E}{RT}}$, which is the maximum rate possible for activation by black body radiation, is only one-millionth of the observed values Several attempts have been made to avoid this difficulty Perrin[3] suggests that the light quantum is re-emitted after decomposition of the active molecule and passes on to the next If this hypothesis were true it is difficult to see why the same phenomenon does not occur in true photochemical reactions where a number of cases of the Einstein law of photo-equivalence have been found. Tolman[4] and Rideal[5] assume that the whole of the inflowing radiation is available for activation. Such an operation can be imagined to proceed by considering the activation of molecules to take place in steps, by absorption of smaller quanta, there being a number of stages corresponding to a number of absorption lines in the spectrum of the substance. This conception, together with the assumption that absorption of the energy in a particular part of the spectrum is accompanied by a rapid redistribution of energy so as to give the typical black body energy wave-length curve, accounts, as Tolman has shown, for the existence of a temperature coefficient of photochemical actions. We may note, for example, in the case of the decomposition of oxalacetic ester at 18·3° the energy necessary for activation was found to be 3·0 10^6 ergs per c.c. per second, whilst the total energy in a black body enclosure per cubic centimetre is given by Stefan's equation

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[1] *J Amer Chem Soc*, 1925, **47**, 1543, *Phys Rev*, 1924, 23643

[2] Dushman, *J Amer Chem Soc*, 1921, **43**, 397

[3] *Trans Farad Soc*, 1922, **17**, 605

[4] *J Amer Chem Soc*, 1920, **42**, 2506, 1925, **17**, 1526

[5] *Trans Farad Soc*, 1922, **17**, 605.

$$E = 3{\cdot}72\ 10^{-5}T^4 \text{ or } 2{\cdot}4\ 10^6 \text{ ergs. at } 183^\circ \text{ C.}$$

This view, in a slightly different form, has been advanced by G. N. Lewis and Smith,[1] who have calculated on the hypothesis of discrete quanta of cross-sectional area $A = \frac{\lambda^2}{8\pi}$,[2] the probability of collision between molecules and quanta, the former possessing a certain internal energy e, and the latter of frequency ν, such that $e + h\nu' = \epsilon_c$.

The chance ϕ' that a molecule will encounter a quantum moving with the velocity of light c of any frequency above a given frequency ν' is found to be

$$\phi' = \int_{\nu'}^{L} A\ c\frac{\partial\rho}{\partial\nu}\delta\nu.$$

where

$$\frac{\partial\rho}{\partial\nu} = \frac{\rho\nu}{h\nu} = \frac{8\pi\nu^2}{c^3}e^{-\frac{h\nu}{kT}},$$

whence

$$\phi' = \frac{kT}{h}e^{\frac{h\nu'}{kT}}.$$

The chance that a molecule possessing internal energy e will encounter a quantum of frequency higher than ν' in unit time will be

$$d\rho = \phi'\frac{dw}{de}de,$$

where $\frac{dw}{de}$ is the fraction of molecules having internal energy between e and $e + de$.

Hence the chance P that a molecule chosen at random will in unit time meet a quantum which has sufficient energy to take the molecule from the unactivated to the activated state.

$$\rho = \int_E^{E_c}\phi\frac{dw}{de}de = \frac{kT}{Eh}\int e^{\frac{E-E_c}{RT}}\cdot\frac{dw}{de}de,$$

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[1] *J. Amer. Chem. Soc.*, 1925, **47**, 1519.

[2] See also Rideal, *Phil. Mag.*, 1920, **40**, 463.

where e is the internal energy of the molecule and e_c the critical value. *In a molecular system possessing no internal energy except that of rotation with two degrees of freedom we obtain*

$$\frac{dw}{de}=\frac{1}{kT}e^{-\frac{E}{kT}},$$

whence

$$\rho=\frac{E_c}{h}e^{-\frac{E_c}{kT}},$$

an equation originally suggested by Dushman and Rideal

A similar equation can be developed for molecules possessing more than two degrees of freedom

It will be noted that these modifications of the original hypothesis are in essentials somewhat similar, in that a part of the necessary critical energy increment is already present as internal energy in a molecule undergoing activation, whilst Tolman would suggest that all internal energy is supplied by radiation, G N Lewis merely postulates its existence and sees in this a part of the energy necessary for activation

On the redistribution of internal energy as a mechanism of activation.—In the preceding section we have examined the various attempts which have been made to reconcile the experimental rates of reaction with the hypothesis that the energy of activation is supplied by the inflow of black body radiation The outcome can scarcely be regarded as satisfactory, and in consequence many have rejected the radiation theory *in toto* and have fallen back on the theory of activation by collision, which we shall have occasion to discuss in the next section. Before this attitude can be justified it is clearly necessary to show that there are no unimolecular chemical reactions, because, although the original conception of Perrin, Trautz, and McC Lewis that the inflowing radiation was the source of activation may be erroneous, the very existence of a true unimolecular reaction certainly demands an explanation in terms of some type of interaction between radiation and matter

The only definite example of a well-established case of unimolecular decomposition is that of nitrogen pentoxide, although many cases of evaporation and sublimation,[1] and, within certain limited temperature ranges, the thermal decomposition of sulphuryl chloride,[2] likewise conform to a reaction rate of the first order.

The decomposition of nitrogen pentoxide has been the subject of numerous investigations by Daniels and his co-workers,[3] Lueck,[4] White and Tolman,[5] Hirst,[6] and Hirst and Rideal[7] It is found that from high pressures down to *ca.* 0·25 mm. the reaction velocity may be expressed in the form

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[1] Rideal, *Proc. Camb Phil Soc*, 1921, **26**, 241

[2] Smith, *J Amer Chem Soc*, 1925, **47**, 1862

[3] *J. Amer Chem Soc*, 1921, **43**, 53; *ibid*, 1922, **44**, 2402, *ibid*, 1925, **47**, 1602.

[4] *Ibid.*, 1922, **44**, 757.

[5] *Ibid*, 1925, **47**, 1240.

[6] *J. Chem. Soc*, 1925, **127**, 657.

[7] *Proc. Roy Soc*. 1925. **109A**. 528.

$$-\frac{dc}{dt}=4{\cdot}98\,.\,10^{13}e^{-\frac{24,700}{RT}}c,$$

viz. the mean value determined from the data of Daniels and Hirst; below 0·25 mm. the reaction velocity increases to a limiting value at considerably smaller pressures where the reaction rate is a little over five times that at high pressures, or

$$-\frac{dc}{dt}=2{\cdot}53\,.\,10^{14}e^{-\frac{24,700}{RT}}c,$$

a value in close agreement with that given by the equation of Dushman[1] and Rideal,[2]

$$-\frac{dc}{dt}=\nu e^{-\frac{Nh\nu}{RT}}c=2{\cdot}59\,.\,10^{14}e^{-\frac{24,700}{RT}}c$$

Between the pressures of 0·25 mm and the smaller values the reaction velocity constant increases, and it was shown by Hirst and Rideal that the experimental data were in agreement with the hypothesis that, of the total number of active molecules present at any time, viz. $Ne^{-\frac{Nh\nu}{RT}}$, one-fifth of them decomposed at once, but four-fifths of them had to remain in the active state without suffering deactivating collision for $9{\cdot}5\,.\,10^{-7}$ seconds before decomposition occurred, the velocity of decomposition being expressible in the form

$$-\frac{dc}{dt}=4{\cdot}98\,.\,10^{13}\left\{1+4{\cdot}09e^{-1{\cdot}063P}\right\}e^{-\frac{24,700}{RT}}c,$$

where P is the pressure in millimetres and $e^{-1{\cdot}063P}$ the fraction of the active molecules having a life of $9{\cdot}5\,.\,10^{-7}$ seconds.[3] The possibility of the energy of activation being resident in any one of the five NO groups of the N_2O_5 molecule, and of decomposition only taking place on activation of one particular group, the time necessary for the energy to leave one $-NO$ group and enter the particular group being $9{\cdot}5\,.\,10^{-7}$ seconds, immediately suggest themselves as a plausible explanation why some molecules require a "life" before decomposition. It is clear that the decomposition of nitrogen pentoxide is unimolecular in character down to pressures so low that explanations on the hypothesis of activation by any form of molecular impact are not very probable. At the same time the inflowing radiation is inadequate to provide the necessary energy.

We may note that, if the decomposing gas were confined in a radiation impermeable envelope, at any moment the rate of decomposition of molecules with the concomitant liberation of internal energy

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[1] *J. Amer. Chem. Soc.*, 1921, **43**, 397.

[2] *Phil. Mag.*, 1920, **40**, 461.

[3] Cf. Jeans, *Dynamical Theory of Gases*, p. 258.

of activation would be equal to the rate of formation of new active molecules, this rate of decomposition and formation being given by the equation referred to above. Thus, no supply of new energy of activation is required, merely a redistribution of internal energy amongst the molecules

In the particular degree of freedom, comprising one of the oscillators in the molecule, which, on activation, causes molecular disruption, there is at any temperature, on the average, RT calories. This average value, however, is not the result of equal distribution amongst all the molecules, but the various molecules differ from one another in the possession of different numbers of quanta, those possessing such a number that the energy content in this degree of freedom is $Nh\nu$ or 24,700 calories per grm.-mol. are said to be activated. We may logically infer that the energy of activation is already present inside the molecules as internal energy, being originally supplied by infra-elastic collision, a method which we shall discuss in the next section. We must therefore examine the various methods by which the distribution of this internal energy can be effected amongst the various molecules It is clear that the usual method of redistribution by molecular collision is much too slow to effect activation at the necessary rate, some type of "quantum sprung" postulated by Polanyi[1] is clearly necessary, but the mechanism by which a quantum liberated by a decomposing molecule is absorbed by another is by no means clear

The data of Warburg and Leithauser[2] show a number of absorption bands for nitrogen pentoxide between 2·4 and 8·7μ, with a particularly strong line at 5·81 which is five times that calculated from the critical energy movement, viz 1·16μ, the possibility of the redistribution of the energy of the internal specific heat by the emission and absorption of quanta of small size is thus not negatived by spectroscopic evidence. Two difficulties, however, have to be overcome in this conception, If we imagine a molecule possessing, say, two quanta, it is evident that this molecule can either receive another or loose one, it may in fact become a creditor or debtor molecule The conditions under which a molecule may become a creditor or debtor must be governed by some type of fluctuation not connected with molecular impact; it is possible that the radiation flowing in the system may render molecules oscillating in phase with it creditors and those out of phase debtors Again, on the assumption of the passage of quanta from molecule to molecule it is necessary that the absorption coefficient be extraordinarily large, for the inflowing and eflowing radiation of these wave-lengths is but a very small fraction of the number of quanta flowing from molecule to molecule within the system The absorption coefficient in those cases must be much larger than those experimentally observed for fluorescent radiation, and we are led to the conception of the interlinkage (in the manner suggested by Sir J. J. Thomson) of the moving molecules with one another by Faraday tubes along which the quanta flow. It is generally assumed that the quantum cross-sectional area grows with the wave-length ($A\alpha\lambda^2$); thus, the volume of space swept out by a quantum in its motion increases rapidly as we proceed into the infra-red portion of the spectrum; the opportunity of collision with molecules is thus enhanced. Since the wave-length $5{\cdot}81\mu$ is some twenty times that of the resonance line in mercury vapour (2540 A°), the opportunity of collision with molecules and thus the coefficient of absorption will on this view be some four hundred times greater. On analogy with the case cited by Lewis and Smith,[1] the lowest pressure at which the decomposition of N_2O_5 has been examined is 0·05 mm., which is about one hundred times greater than the pressure at which Wood examined the absorption of the line 2540 A° by mercury vapour. A 50 per cent absorption would take place in a layer of *ca.* 0·05 mm. if the coefficient of absorption were equally great as for mercury vapour. If the coefficient is four hundred times greater it is clear that virtually complete absorption of the radiation continually emitted by the molecules in the gas will occur.

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[1] *Zeitsch f Physik*, 1920, I 337, *ibid*, 1920, II. 90, 1920, III.

The theory of activation by collision.—We have noted the simple radiation theory of chemical action is certainly not tenable, and that many drastic amplifications are required before this attractive conception can be made reconcilable with experimental data. The somewhat arbitrary hypotheses necessary for this purpose have led many to reject *in toto* the conception of activation by radiation and to inquire how far it is possible to assume activation by collision. According to this view, when molecules impinging on one another with such initial speeds that the available energy in the case of a simple bimolecular reaction between molecules of mass m exceeds the critical energy increment, or

$$\tfrac{1}{4}mV^2 > E_C,$$

they do not suffer elastic collision but undergo activation and disruption.[2] The data of Hinshelwood and Pritchard, on the bimolecular decomposition of chlorine monoxide,[3] of nitrous oxide,[4] and of Bodenstein on hydrogen iodide,[5] strongly support this view.

Thus, in the case of nitrous oxide decomposition, the rate is found to be expressible between the temperature range 838° K to 1125° K by means of the following equations:

$$-\frac{dc}{dt} = Kc^2 \qquad K = 7{\cdot}60 . 10^{12}\sqrt{T}\, e^{-\frac{58,450}{RT}},$$

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[1] *Loc. cit.*

[2] Lindemann, *Trans. Farad. Soc.*, 1922, **17**, 598.

[3] *J. Chem. Soc.*, 1923, **123**, 2730.

[4] Hinshelwood and Burk, *Proc. Roy Soc.*, 1924, **106A**, 284.

[5] Bodenstein, *Zeitsch. physikal. Chem.*, 1924, **124**, 233.

where 58,480 cals is the energy of activation per two grm.-mols of the gas. The rate of activation by collision is given by the kinetic theory

$$\frac{dA_c}{dt} = Nc^2\sigma^2\sqrt{\frac{4\pi RT}{17}}\,e^{-\frac{E}{RT}},$$

where σ is the molecular diameter.

If we adopt a value of $\sigma = 3.32 \times 10^{-8}$ cm we obtain for the rate of activation by collision

$$\frac{dA_c}{dt} = c^2\,3.25 \times 10^{12}\sqrt{T}\,e^{-\frac{58\,450}{RT}},$$

since two molecules disappear as the result of each such collision the rate of decomposition is clearly

$$-\frac{dc}{dt} = 6.50 \times 10^{12}\sqrt{T}\,e^{-\frac{58\,450}{RT}}c^2,$$

a value so close to that experimentally obtained that there can be little doubt that this hypothesis does provide an adequate explanation for the mechanism of bimolecular reactions, and that no other means of activation is required.

If infra-elastic collisions take place, it is necessary also that supra-elastic collisions occur at the same time; thus, if we imagine molecules becoming activated by the conversion of kinetic energy lost on impact into eternal energy in the quantised form, we must at the same time postulate the contact of an activated molecule with a normal molecule resulting in the reliberation of the internal energy in the kinetic form (a collision of the third kind, to continue the somewhat unsatisfactory classification of collision types). Thus, if the average kinetic energy of each molecule before collision be e and one molecule possess internal energy of activation e^1, the average kinetic energy after collision will be e' such that

$$2e' = 2e + e^1$$

Whilst the existence of infra-elastic and supra-elastic collisions have been well established in a number of cases of electron-molecule impacts, the experiments on activation by molecular collision, which is the basis of this mechanism of chemical change, are more limited. Franck and his co-workers[1] have demonstrated the transfer of internal energy from one molecule to chemical energy in another by effecting the dissociation of hydrogen molecules ($E = 90{,}000$ cals.) with the aid of excited mercury atoms. They have also shown that, at 300° C., excited mercury atoms will, when mixed with thallium vapour, cause the emission of the characteristic thallium line, corresponding to an excitation of 6·1 volts. Since the excited atom is only at a level

[1] Cario, *Zeitsch. f. Physik*, 1922, **9**, 259; 1923, **12**, 162.

corresponding to 5·8 volts it is clear that an additional supply of internal energy equivalent to 0·3 volt (1 volt fall is equivalent to 22,900 calories) must have been supplied by the infra-elastic collision between an excited mercury atom and a normal thallium atom.

Reaction chains and the concept of hot molecules.—In many photochemical actions the Einstein law of photoequivalence is not obeyed, and a ready interpretation of many of these was given by Nernst. According to Nernst, the photochemical combination of hydrogen and chlorine consists in the primary photochemical formation of chlorine and hydrogen atoms from their respective molecules, and this in turn is followed by a series of reactions such as

$$\begin{gathered}Cl + H_2 = HCl + H,\\ H + Cl_2 = HCl + Cl\end{gathered}$$

There is some evidence, due to Norrish, that such atom chains may commence on the walls of the reaction vessel and proceed through the gas phase until they strike the wall again. Both chlorine atoms and hydrogen atoms are immobilised on the walls and may there react with atoms of like or opposite kind. We shall have occasion to discuss the action of the mechanism and the influence of catalysts on these reactions in more detail in a later section.

Christiansen and Kramers [1] have attempted to extend this conception to systems in which *atom* chains are not possible. According to their view, the product of decomposition of a molecule after excitation must possess in itself the original energy of excitation and either an addition or a diminution equal to the heat of reaction. If the reaction be exothermic of value q per molecule the total energy of the product will be

$$h\nu + \tfrac{1}{2}mc^2 + q,$$

where $h\nu$ is the energy of activation, c the molecular velocity, and q the heat of reaction.

The molecules thus possess much more energy than their neighbours; the authors do not commit themselves as to how this energy is stored in these fresh products of reaction, but it would appear that they envisage the probability of "hot" molecules or the energy is in the kinetic form. These "hot" molecules can, by impact, activate by collision of the second kind another reactant molecule, and thus give rise to reaction chains.

The presence of inert gases is frequently without influence on the reaction rate and reactions may also proceed in solution, *e.g.* the decomposition of hydrogen peroxide or nitrogen pentoxide; thus, the hypothesis of kinetically "hot" molecules would appear to be excluded. Again, the view that the energy, if internal, can only be handed on to a reactant and not to a diluent or solvent molecule, assumes that a vibration frequency is common to both reactant and product, an assumption that still awaits experimental verification The suggestion, however, is not without interest, for such a mechanism has been shown by Watson in the following manner to give rise to pseudo-unimolecular constants

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[1] *Loc. cit.*

Arrhenius has expressed the opinion that there is a dynamic equilibrium between the inactive and active molecules, the latter existing in but small quantities We may consequently write

$$C_a = \alpha C_n, \qquad (1)$$

where C_a is the concentration of active molecules,
C_n those of the inactive molecules,
α a small factor

If the active product molecules are the main factor in activation then the concentration of active molecules will be determined by the product of normal molecules C_n and the number of such activating molecules C_a', or

$$C_a = \alpha' C_n C_a' \qquad (2)$$

The query then arises, Under what conditions are these two equations compatible with a unimolecular reaction defined by the expression

$$k = -\frac{1}{C_n}\frac{dC_n}{dt},$$

We may represent our reacting system diagrammatically as follows

$$n \rightleftarrows a \rightarrow a',$$

the first reversible expression representing the Arrhenius equilibrium between normal and active molecules, the second the irreversible decomposition of the active molecules, which is assumed to take place sufficiently slowly as not to effect the equilibrium $n \rightleftarrows a$

The rate of decrease of the normal molecules must be equal to the rate of increase of the active molecules plus the rate of spontaneous decomposition of the a molecules into the products a',

or $$-\frac{dC_n}{dt} = \frac{dC_a}{dt} + SC_a, \qquad (3)$$

where $\frac{1}{S}$ is the mean life of an active molecule

From (1) $$\frac{dC_a}{dt} = \alpha\frac{dC_n}{dt},$$

$$-\frac{dC_n}{dt} = \alpha\frac{dC_n}{dt} + S\alpha C_n.$$

i e. $$-\frac{dC_n}{dt}(1+\alpha) = S\alpha C_n$$

$$-\frac{1}{C_n}\frac{dC_n}{dt} = \frac{S\alpha}{1+\alpha} = \text{a constant at constant temperature} \quad . \quad (4)$$

We have already noted that Marcelin showed that the ratio

$$\frac{C_a}{C_n} = e^{-\frac{E}{RT}}.$$

This expression has been modified by Einstein[1] to the form

$$\frac{C_a}{C_n} = \frac{P_a}{P_n} e^{-\frac{E}{RT}},$$

where P_a, P_n are the *à priori* probabilities of the molecule existing in the active or normal state. In general $P_a = P_n$. Similar considerations hold when the "normal" state is also active (a''), or

$$\frac{C_a}{C_a''} = \frac{P_a}{P_a''} e^{-\frac{(E-E'')}{RT}}.$$

where E and E'' are the energies of activation in each state.

Replacing this value of $\frac{C_a}{C_n} = \alpha$ in (1),

$$\frac{1}{C_n}\frac{dC_n}{dt} = \frac{Se^{-\frac{E}{RT}}}{1+e^{-\frac{E}{RT}}} = Se^{-\frac{E}{RT}}, \quad . \quad . \quad . \quad (5)$$

since α is small by hypothesis; and we thus obtain our original equation which we have already noted as applicable to unimolecular reactions.

From Equation (4) we may evidently obtain the ratio of active to inactive molecules in the Arrhenius equilibrium mixture from a knowledge of k and s. For the decomposition of nitrogen pentoxide $k = 487 . 10^{-3}$ and $s = 10^{14}$ or α the ratio is *ca.* 10^{-17}.

Such a mechanism as has been postulated by Christiansen and Kramers leads to the general expression of a unimolecular reaction in which S is now accurately defined as the probability that an active molecule will decompose within the next second, *i.e.* $\frac{1}{S}$ is the average life.

It has been assumed for this purpose that the active molecule at the moment of decomposition or just after decomposition hands on its energy to activate a new molecule. It is possible that the products of decomposition which are active at the moment of production may, before they relapse into the normal products, likewise impart their energy by collision and thus give rise to reaction chains. Watson has obtained in the following manner the conditions that the reaction should be unimolecular.

There are two possible cases which may be represented diagrammatically as follows:

$$(1) \quad n \rightleftarrows a \rightarrow a' \rightleftarrows n'.$$

$$(2) \quad n \rightleftarrows a \longrightarrow a' \rightarrow n'.$$

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[1] *Physikal. Zeitsch.*, 1917, **18**, 121

In the first case the deactivated products are in equilibrium with the activated products (7) $C_a' = \beta C_n'$ where β is small, and, in the second case, the deactivation of the products is irreversible We can investigate the nature of the reaction in a way similar to that indicated above

Case (1) Reversible equilibrium between active and inactive products assumed

As before $$-\frac{dC_n}{dt} = \frac{dC_a}{dt} + SC_a, \qquad (3)$$

and applying the same idea to the active products,

$$-\frac{dC_n'}{dt} = SC_a - \frac{dC_a'}{dt} \qquad (8)$$

Finally $C_a = \alpha' C_n C_a'$ (2) from our initial assumption

From (7) and (2) $$\frac{dC_a'}{dt} = \beta\frac{dC_n'}{dt} \qquad (9)$$

and $$\frac{dC_a}{dt} = \alpha' C_n \frac{dC_a'}{dt} + \alpha' C_a' \frac{dC_n}{dt} \qquad (10)$$

From (9) and (8) we obtain $\frac{1}{\beta}\frac{dC_a'}{dt} = SC_a - \frac{dC_a'}{dt}$

or $$\frac{dC_a'}{dt} = \frac{SC_a}{1+\frac{1}{\beta}} = \frac{\beta SC_a}{1+\beta} \qquad (11)$$

Substituting (2) and (11) in (10) we obtain

$$\frac{dC_a}{dt} = \alpha' C_n \frac{\beta SC_a}{1+\beta} + \frac{C_a}{C_n}\frac{dC_n}{dt} \qquad (12)$$

Substituting the value of $\frac{dC_a}{dt}$ obtained in (3),

$$-\frac{dC_n}{dt} = SC_a - \frac{\alpha'\beta S}{1+\beta} + \frac{C_a}{C_n}\frac{dC_n}{dt}$$

or $$-\frac{dC_n}{dt} = \frac{SC_a - \frac{\alpha'\beta S}{1+\beta}C_aC_n}{1+\frac{C_a}{C_n}}$$

∴ the unimolecular constant K is

$$-\frac{1}{C_n}\frac{dC_n}{dt} = \frac{S\frac{C_a}{C_n} + \frac{\alpha'\beta S}{1+\beta}SC_a}{1+\frac{C_a}{C_n}},$$

since $\frac{C_a}{C_n} = \alpha$ and β are small compared with unity by hypothesis,

$$K = S\frac{C_a}{C_n} + \alpha'\beta S C_a - S\alpha'(C_a' + \beta C_a). \quad . \quad . \quad (13)$$

If C_a and C_a' are of the same order of magnitude and small,

$$K = S\alpha' C_n' = S\alpha'\beta C_n'$$

Thus, the unimolecular constant is directly proportional to the concentration C_n' of the molecules formed by the change, *i.e.* the reaction is autocatalytic.

Thus, an autocatalytic reaction will be obtained where

$$K' = \frac{1}{C_n C_n'}\frac{dC_n}{dt} \text{ or } \frac{dC_n}{dt} = K'(C_a - C_n)C_n$$

Evidently for such a reaction to give a unimolecular constant C_n must be a constant, or from (7) C_n' must be a constant, which from (2) we see that this is equivalent to postulating the existence of the equilibrium demanded by Arrhenius:

$$C_a = \text{Constant } C_n$$

Case (2). In this case deactivation of the products is assumed to take place irreversibly or $n \rightleftarrows a \rightarrow a' \rightarrow n'$.

As before from (2)

$$C_a = \alpha' C_n C_a'. \quad . \quad (2)$$

$$-\frac{dC_n}{dt} = \frac{dC_a}{dt} + SC_a \quad (3)$$

We have also
$$-\frac{dC_a'}{dt} = S'C_a' - SC_a. \quad . \quad . \quad . \quad (14)$$

where a' is supposed to decompose spontaneously and in a unimolecular manner with velocity S'.

On differentiating (2) as before with respect to t we obtain

$$\frac{dC_a}{dt} = \alpha' C_n \frac{dC_a'}{dt} + \alpha' C_a' \frac{dC_n}{dt}. \quad . \quad . \quad (10)$$

from (3) + (10)

$$-\frac{dC_n}{dt} - SC_a = \alpha' C_n(-S'C_a' + SC_a) + \alpha' C_a' \frac{dC_n}{dt},$$

i.e.
$$\frac{dC_n}{dt}(1 + \alpha' C_a') = -SC_a + \alpha' S' C_n C_a' - \alpha' S C_n C_a,$$

from (2)
$$= -S\alpha' C_n C_a' + \alpha' S' C_n C_a' - \alpha'^2 S C_n^2 C_a',$$

i.e.
$$\frac{1}{C_n}\frac{dC_n}{dt} = \frac{\alpha' C_a'(-S + S' - \alpha' S C_a)}{1 + \alpha' C_a'}.$$

The problem is to find under what conditions this will be a constant. If the change $a \longrightarrow a'$ is much quicker than from $a' \longrightarrow n'$ then $\frac{C_a}{C_n'}$ and therefore $\alpha' C_n$ will be small in comparison with unity, and we know already that $\alpha' C_a' \frac{C_a}{C_n}$ is small compared with unity

Hence
$$K = -\frac{1}{C_n}\frac{dC_n}{dt} = \alpha' C_a'(S - S') = \alpha' C_a' S,$$

since S is much greater than s in the above assumption

The a molecules are in the same position as a radioactive element, and therefore when the reaction is proceeding steadily C_a is constant and the reaction will be unimolecular again, however, by (2), this leads to the existence of an Arrhenius mass equilibrium between active and inactive molecules, or $\frac{C_a}{C_n} = \alpha' C_a'$ Constant

In that case we have assumed that the change $a' \longrightarrow n'$ is slower than the change $a \longrightarrow a'$ which in turn is already assumed much slower than the change $n \longrightarrow a$ or $a \longrightarrow n$, or the deactivation of the active product is required to be very much slower than the deactivation of the active reactant Such conditions are evidently fulfilled, according to Tolman's calculations,[1] when the energy of activation of the reactant is much larger than the energy of activation of the product

Watson has summarised the conclusions drawn from this development of the hypothesis of Christiansen and Kramers as follows

(1) If the energy of activation be acquired from highly energised reaction products the reaction will be unimolecular in type only if there exists a simple proportionality between the concentration of active and inactive molecules, as postulated by Arrhenius

(2) If the deactivation of the active products takes place reversibly the reaction will be, in general autocatalytic

(3) If the deactivation be spontaneous and irreversible, the law will be that of a unimolecular reaction provided that the deactivation is much slower than the loss of energy by the active resultant

It must be admitted that this attractive conception of chain mechanism still awaits exact experimental confirmation

Active molecules. Although the arguments are by no means conclusive, there are strong reasons for assuming that the active molecules postulated by Arrhenius are identical with the "excited" molecules of the physicist The distortion of the molecule or the quantity of energy required to send the electron to its new orbit is, for most chemical processes, much smaller than those which have been made the subject of experimental physical research, for, in general, the wave-length of the equivalent quantum of energy is confined to the infra-red portion of the spectrum. Further, we must assume that molecular excitation may be produced not only by the usual methods of absorption of radiation or by collision with α-particles or electrons, but also by molecular collision.

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[1] *Loc cit*

The lives of excited molecules.—Experimental determinations of the time of emission of radiation have been made by Wien[1] and Dempster,[2] and periods have been calculated by Milne,[3] Stern and Vollmer,[4] Turner[5] and Tolman,[6] Saha,[7] Weigert and Kellermann.[8] The following observed and calculated values are obtained:

	Experimental		Calculated	
Hg	1·03 . 10^{-7} sec.	I_2	(λ 5461)	2·94 . 10^{-3} sec.
Hβ	5·0 . 10^{-8} ,,	HCl	(λ 32340)	0·0174 sec.
Hχ	2·0 . 10^{-8} ,,	HCl	(λ 34150)	0·829 sec.

The experimental values for τ for excitation in visible light are all of the order of 10^{-7} seconds, whilst those calculated on the correspondence principle increase very rapidly as the energy of the quantum decreases; this increase has not, however, yet received any experimental confirmation. Since, in the majority of chemical actions, the energies of activation involved are relatively small, it is a matter of great importance to find out whether the long lives anticipated by Tolman for molecules activated by collisions of the second kind do actually exist.

The original experimental equation of Arrhenius may be integrated in the following form:

$$\log_e K = -\frac{E}{RT} + C$$

or

$$K = e^C e^{-\frac{E}{RT}}.$$

If C be the integration constant, e^C may be replaced by S where

$C = \log_e S$, whence $$K = Se^{-\frac{E}{RT}}.$$

It is clear that if the term $e^{-\frac{E}{RT}}$ represents the fraction of excited or active molecules, S has consequently the dimensions of a frequency, and is regarded by many as the reciprocal of the time (τ) necessary for the molecule to pass from the active or excited to the inactive or passive condition.

Others have suggested[9] that this time is not the time required for the emission of its internal energy as radiation but represents rather the average time before a crisis occurs in the active molecule. At this crisis the molecule either undergoes chemical reaction or commences to revert to the normal form. These crises are possibly connected with the position of the electron in its unstable orbit, since its frequency is given by the expression $E = Nh\nu$, we obtain $S = \nu$ or $K = \nu e^{-\frac{E}{RT}}$. Amongst other suggestions it has been proposed that $\frac{1}{S}$ represents a time period $\frac{1}{\nu'}$, where ν' is a frequency of the molecule, but not necessarily that derived from the temperature coefficient.[1] It may be noted in passing that 10^{-14} seconds, which is of the same order as ν for ultra-violet frequencies, is also the computed period of the duration of an elastic collision.

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[1] *Ann. Physik*, 1919, **60**, 597 ; 1921, **66**, 229.

[2] *Phys. Rev.*, 1920, **15**, 158.

[3] *Proc. Camb. Phil. Soc.*, 1925, **22**, 493.

[4] *Physikal. Zeitsch.*, 1919, **20**, 183.

[5] *Phys. Rev.*, 1924, 2, **23**, 464.

[6] *Ibid.*, 1924, **23**, 693

[7] *Phil. Mag.*, 1924, 6, **48**, 421.

[8] *Zeitsch. physikal. Chem.*, 1923, **107**, 1.

[9] Dushman, *J. Franklin Inst.*, 1920, **189**, 515 ; *J. Amer. Chem. Soc.*, 1921, **43**, 403 ; Rideal, *Phil. Mag.*, 1920, **40**, 462

The energies of activation in the presence of catalysts. A number of cases have been examined on the alteration of the velocity constant as well as of the temperature coefficient of a chemical reaction when either reacting molecule possesses different substituent groups or various solvents are employed. Whilst the reactions are undoubtedly complex and deductions based on an assumed simplicity are open to criticism, nevertheless some interesting relationships have been obtained.

Nicoll and Cain[2] have examined the rate of decomposition of the substituted diazobenzene chlorides in excess of water according to the reaction

$$RC_6H_4N_2Cl + H_2O \longrightarrow RC_6H_4OH + N_2HCl$$

The reaction is pseudo-unimolecular and can be expressed in the form

$$-\frac{1}{c}\frac{dc}{dt} = Se^{-\frac{E}{RT}}$$

That a formal relationship between S and E exists has been pointed out by Watson and is evident from the following data

Substituent group R	E cals per grm mol	$\log_{10} S$	$\frac{E}{\log_{10} S}$
H	24,300	13.6	1790
o-CH_3	25,100	14.6	1720
m-CH_3	22,900	13.0	1760
p.-CH_3	27,900	15.0	1860
p-SO_3H	28,200	14.9	1890
m-NO_2	30,500	15.0	2030

The value of E likewise changes in the case of the substituted oxalacetic esters (EtOOC·CO·CHR·COOEt) examined by Watson, which undergo decomposition in a pseudo-unimolecular manner

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[1] Christiansen *Zeitsch physikal Chem*, 1922, **103**, 91

[2] *J Chem Soc*, 1903, **83** 470

Substituent group R.	E cals per grm.-mol.	$\log_{10} S$	$\frac{E}{\log_{10} S}$
$-OC_2H_5$	33,800	13·94	257
CH_3	33,300	13·36	249
$-CH_2COOC_2H_5$	35,400	14·30	247
C_6H_5	44,300	19·88	223

Alterations in E may likewise be produced when instead of altering the molecular structure of the reactant, we change the solvent, the influence of which we shall discuss in a subsequent section. The following data, calculated from Cox, on the addition of aniline to bromacetophenone,[1] may be cited in this connection:

Solvent	E cals	k 37·8° C
C_6H_6	8,088	·000985
CCl_3H	10,760	·00186
$C_6H_5NO_2$	13,470	·0135
CH_3COCH_3	11,080	·0764
$C_6H_5CH_2OH$	14,290	·0440
N. butyl alcohol	14,060	0550
Ethyl alcohol	13,910	·0626
Methyl alcohol	12,440	0748

Similar alterations of the critical increment with the solvent may be noted in the data of von Halban[2] for triethyl sulphine bromide, and of Dimroth[3] on the decomposition of the methyl ester of benzyl 5, hydroxy 123, triazole benzoate

Decomposition of Triethyl Sulphine Bromide.		Decomposition of the Triazole Benzoate	
Solvent	E cals	Solvent	E cals
Nitrobenzene	28,330	Acetone	29,140
Tetrachlorethane	30,390	Ethyl alcohol	30,640
Iso-amyl alcohol	33,190	Chloroform	35,420
N. propyl alcohol	33,750		
Benzyl alcohol	75,920		

We note that the energies of activation are definitely affected by solvents; it is for this reason that the theoretical considerations advanced in the preceding paragraphs are of importance in the study of catalytic reactions both homogeneous and heterogeneous. Evidence is slowly accumulating that it is to the catalytic agent that we must turn if it is desired to reduce the energy increment necessary to produce a certain reaction process. In all probability the initial process in the catalysis is a deformation of the structure of the molecule by association with the catalytic agent, either as a molecular complex or compound in homogeneous catalysis or as an adsorbed atom or molecule on a contact catalyst. That such association materially alters the energy required for reaction to occur is to be concluded from recent studies in the domain of photochemistry, and especially in the hydrogen-chlorine combination. An examination, by Coehn and his co-workers,[1] of the insensitivity of dry hydrogen-chlorine mixtures to visible light has indicated such a conclusion. They have shown that whereas moist mixtures of these two gases are photosensitive in the blue region of the spectrum, the gas mixtures in which the water-vapour pressure is of the order of 10^{-7} mm. are first sensitive in the ultra-violet region below $\lambda = 3000$ A°. The energy quantities involved are respectively about 52,500 cals. in the water catalysed reaction and 94,500 cals. in the non-catalysed reaction.

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[1] *J. Chem. Soc.*, 1921, **119**, 142.

[2] *Loc. cit.*

[3] *Lieb. Ann.* **373**, 336, 1910.

Homogeneous reactions in solutions.—The considerations advanced in the preceding sections may be applied to the more complicated cases of liquids. We have noted that unimolecular reactions in gaseous systems are extremely rare and must conclude that the same is true in solution; thus, cases of dynamic isomerism, *e.g.* acetoacetic ester, cannot be satisfactorily explained on the hypothesis of an intramolecular reaction, although this view is still maintained by some investigators. In solutions, also, complexes or solvates may be formed; the study of bimolecular reactions in gases indicates a possibility that the reaction of tautomeric change may take place through activation by collision between solvent and solute molecule, but, as we shall note, the critical energy increment is high and the reaction velocity negligible at ordinary temperatures. It is for this reason that it is probable that most reactions in solution occur through the intermediary of ternary complexes, reactant, solvent, catalyst. In order to justify this point of view, we must determine the evidence in favour both of the existence of such complexes and also why such complexes are more easily activated and thus undergo reaction more readily than the simpler binary constituents also present in the system.

To obtain some idea of the mechanism of such reactions we must examine both the form of the reaction velocity concentration relationships and the influence of temperature on the velocity coefficient. It is found in the majority of cases that a reaction proceeding in dilute solutions according to the equation

$$a + b \rightarrow d$$

proceeds at a velocity that is proportional to the bulk concentrations,

$$\frac{dx}{dt} = k(a)(b)$$

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[1] *Ber.*, 1923, **56**, 458, 696; *Zeitsch. physikal. Chem.*, 1923, **105**, 356; 1924, **110**, 705.

In more concentrated solutions this equation fails. Whilst Arrhenius, Ostwald, and Euler noted a parallelism between the reaction velocity and the osmotic pressure of the reactant, the more precise conception of thermodynamic concentration introduced by G. N. Lewis has, of later years, been applied to reaction velocities by Harned[1] and McC. Lewis,[2] who suggested that, in lieu of concentrations, the activities or thermodynamic concentrations of the reactants should be employed. The equation then becomes

$$\frac{dx}{dt} = k(a)(b)f_a f_b$$

where $f_a f_b$ are the activity coefficients of the reactants.

Brönsted[3] assumed that the reaction would proceed by the formation of an unstable intermediate complex (ab) which underwent rapid decomposition to the products c or $a + b \xrightarrow{\text{slow}} (ab) \xrightarrow{\text{fast}} c$.

The assumption that the velocity of reaction was determined by the ratio of the activities of the reactants to that of the products leads to the equation

$$\frac{dx}{dt} = k_1(a)(b)\frac{f_a f_b}{f_c}.$$

Bjerrum has criticised this equation[4] from two points of view. Whilst the insertion of activities in lieu of actual concentrations may be justifiable in systems at, or close to, equilibrium, it is probably erroneous to assume that the number of collisions in a system undergoing reaction is influenced by the activities, although the number of effective collisions may be determined by the factor Again, the rate at which the complex (ab) undergoes reaction is not demonstrably influenced by its potential; thus, in radioactive transformation the rate of decay is uninfluenced by the activity of the system.

Bjerrum assumes that the reaction velocity is proportional to the concentration of the complex ab, or

$$\frac{dx}{dt} = k(ab).$$

According to the law of mass we obtain

$$\frac{(a)(b)}{(ab)}\frac{f_a f_b}{f_{(ab)}} = K,$$

where K is the mass action equilibrium constant.

Hence

$$\frac{dx}{dt} = k'\frac{(a)(b)f_a f_b}{f_{(ab)}}.$$

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[1] *J. Amer. Chem. Soc.*, 1918, **40**, 1461.

[2] *J. Chem. Soc.*, 1920, **117**, 1120; 1922, **121**, 1613.

[3] *Zeitsch. physikal. Chem.*, 1922, **102**, 169.

[4] *Ibid.*, 1923, **108**, 85.

On this view the reaction velocity is defined by two terms, the concentration and the stability of a complex. The existence of such complexes in solution, *e.g.* of esters and acids, sugars and water, has been fully demonstrated by the work of Kendall and his co-workers.

The action of catalytic agents in accelerating the reaction velocity of a typical homogeneous reaction is due to the formation of a new complex present in different amount and of different stability to the original. Thus, in the above reaction, if a catalyst of concentration *c* be added, the reaction velocity will be expressed by the equation

$$\frac{dx}{dt} = k'\frac{(a)(b)f_a f_b}{f_{ab}} + k''\frac{(a)(b)(c)f_a f_b f_c}{f_{(abc)}}$$

Whether any reaction proceeds in the absence of a catalytic agent, *e.g.* the mutarotation of sugars or the isomeric change of nitro-camphor or aceto-acetic ester,[1] cannot, of course, be verified experimentally, as results either positive or negative are evidently susceptible to criticism. An examination of the temperature coefficient of catalysed reactions, however, leads one to infer that many reactions virtually do not proceed at all in the absence of catalysts.

The extremes of the temperature coefficients of such catalysed reactions are found to be $\frac{K_{35}}{K_{25}} = 4·13$ for the hydrolysis of cane sugar in the presence of hydrochloric acid, and 1·82 for the hydrolysis of methyl acetate in the presence of caustic soda, corresponding to energies of activation of 26,000 and 10,900 cals. per grm.-mol. respectively. Since the concentration of the ternary complex (*abc*) must be much less than (*ab*), it is clear from the augmentation of the velocity produced on the addition of the catalyst that the fragility or ease of decomposition of this ternary complex must be much greater than that of the binary complex (*ab*), and the energy of activation correspondingly less. We have noted that in cases of bimolecular gas reactions, where activation is caused by collision, the reaction proceeds relatively rapidly when the energies of activation are not too large, as exemplified in the following data obtained by Hinshelwood.[2]

Bimolecular Reaction Decomposition of	E cals. per grm. mol.	T_{ab}	$\frac{E}{T_{ab}}$
$2N_2O$	58,500	956	61
$2HI$	44,000	760	58
$2Cl_2O$	21,000	384	55

In the above table T_{ab} is the temperature at which *k*, the bimolecular velocity coefficient, has the same value for each reaction, viz. $k = 0·0914$ grm.-mol. per litre per second. We may thus anticipate reactions to take place in solution at ordinary temperatures with measurable speeds when the energies of activation are small; the temperature coefficients of the catalysed reactions indicate that the energies of activation of the ternary complexes are of the order anticipated from analogy with the homogeneous kinetically activated gas reactions. The bimolecular reaction $a + b \rightarrow c$, on the other hand, evidently requires a much larger energy of activation, and will thus proceed at ordinary temperatures at rates comparable to, say, the decomposition of nitrous oxide or the union of hydrogen and oxygen at low temperatures. We may conclude that binary complexes may be formed, but reaction does not necessarily result; thus, in the interaction between ethylene and hydrobromic acid, the complex, as shown ($C_2H_4 . HBr$) by Maas, is present at low temperatures in relatively large quantities, but ethyl bromide is not formed, presumably owing to the large value of the critical energy increment.

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[1] Lowry, *J. Chem. Soc.*, 1899, **75**, 211; 1908, **93**, 119.

[2] *J. Chem. Soc.*, 1925, **125**, 1843.

The stability of intermediate compounds. In the foregoing discussion it has been shown that the mechanism of reaction in solutions can be most readily interpreted on the concept of unstable intermediate complexes. Thus, in the reaction $a + b \rightarrow d$ cafalysed by the catalyst c the formation of complexes by a series of reactions $a + b \rightarrow (ab)$, $ab + c \rightarrow (abc)$ is postulated. Whilst reaction may take place without the catalyst by the reaction

$$a + b \rightarrow (ab) \rightarrow d,$$

it would appear that the energies of activation are so large that such reactions do not occur in liquids at ordinary temperatures and the usual mechanism is $a + b \rightarrow (ab)$, $(ab) + c \rightarrow (abc) \rightarrow d + c$, the complex (abc) being very unstable and consequently present in solutions in sub analytical quantities.

Whilst the presence of binary complexes in strong solutions can be readily demonstrated by the various methods commonly employed for this purpose, the identification of the ternary complex which is the one actually undergoing the chemical change being measured is not such a simple matter; for, to take a specific example, we are by no means justified in the assumption that, since Kendall has demonstrated the existence of unstable compounds of the type $RCOOR' . HX$, that a complex $RCOOR'HX . H_2O$ is the actual intermediary complex in catalytic hydrolysis.

Attempts have been made to identify these unstable complexes in two ways. We may either investigate the functional relationship between the reaction velocity and the activities of all the possible reacting species so as to obtain a general expression of the type

$$\frac{dx}{dt} = K' \frac{(a)^n (b)^m (c)^o}{f(a^n b^m c^o)} f_a^n f_b^m f_c^o,$$

or we may develop, from preconceived hypotheses as to the stability of molecules of different configuration, a structure that will be readily susceptible to the reaction desired.

As an example of the former method may be cited the case of hydrogen ion catalysis in a number of reactions such as the inversion of sucrose.[1] This reaction may be regarded as proceeding through the formation of a ternary complex (sugar) · (water ^{n}) · ($\dot{H}$), since the reaction proceeds at a velocity directly proportional to the activities of the two solutes of the system; uncertainty, however, still exists as to the true value of n for the solvent, which different observers evaluate at from 2 to 6. Whilst the activity of the hydrogen ion in solution may be determined by various methods,[2] or calculated from the bulk concentration of reactants with the aid of the equations developed by Noyes and Falk,[3] Lewis and Linhart,[4] Bronsted,[5] Bjerrum,[6] or Debye and Huckel,[7] we cannot from this relationship alone determine whether the hydrogen ion forming the reaction complex is hydrated or not.

Since the equilibrium $\dot{H} + nH_2O \rightleftarrows (\dot{H} \cdot nH_2O)$ or $\dot{H} \cdot aH_2O + bH_2O \rightleftarrows (\dot{H} \cdot nH_2O)$, where $a + b = n$, may be set up in the system, evidently either form of the hydrogen ion is available to form the reactive complex. The investigations of Lapworth[8] and Dawson,[9] as well as the numerous experiments on neutral salt action (see p. 173), have made it more than probable that it is the unhydrated or the less hydrated form of hydrogen ion is the active agent.

Again, we may note that the solvation of sucrose varies but little with the temperature, or the value of (ab) will be constant over a considerable range of temperatures. The influence of temperature on the reaction velocity will thus be largely affected by the change in the concentration of the active form of the hydrogen ion with the temperature, a conclusion arrived at by Rice.[10]

Amongst other examples of this method may be cited the decomposition of acetylchloramino benzene in the presence of hydrochloric acid as a catalyst examined by Rivett[11] and Harned and Selz,[12] and of hydrogen peroxide in the presence of hydrobromic acid examined by Bray and Livingstone,[13] where the reaction velocities of the reactions are expressible in the forms

$$(1) \quad -\frac{dc}{dt} = (C)(\dot{H})(Cl')f\dot{H}fCl',$$

$$(2) \quad -\frac{dc}{dt} = (C)(\dot{H})(Br')f\dot{H}fBr'.$$

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[1] Harned, *J. Amer. Chem. Soc.*, 1915, **37**, 2467; *ibid.*, 1918, **40**, 1461; Fales and Morrell, *ibid.*, 1921, **44**, 2072; McC. Lewis and Corran, *ibid.*, 1921, **44**, 1673; Scatchard, *ibid.*, 1923, **45**, 1580; McC. Lewis and Jones, *J. Chem. Soc.*, 1920, **117**, 124.

[2] Lewis and Randall, *Thermodynamics*.

[3] *J. Amer. Chem. Soc.*, 1910, **32**, 1011.

[4] *J. Amer. Chem. Soc.*, 1919, **41**, 1955.

[5] *J. Amer. Chem. Soc.*, 1922, **44**, 938.

[6] *Zeitsch. f. Elektrochem.*, 1918, **24**, 321.

[7] *Physikal. Zeitsch.*, 1923, **24**, 185, 305.

[8] *J. Chem. Soc.*, 1908, **73**, 2157.

[9] *J. Chem. Soc.*, 1911, 991.

[10] *J. Amer. Chem. Soc.*, 1923, **45**, 2808.

[11] *Zeitsch. physikal. Chem.*, 1913, **82**, 201.

[12] *J. Amer. Chem. Soc.*, 1922, **44**, 1484.

[13] *J. Amer. Chem. Soc.*, 1923, **44**, 1251, 2048.

More speculative in character is the second method of approaching this question from the supposed electrical structure of organic compounds. The problem may be exemplified in the case of the combination of ethylene and chlorine or bromine. At low temperatures these gases do not react by bimolecular collision.[1] Undoubtedly compounds are formed on collision of the type ($C_2H_4 . Br_2$), but the energy of activation is so high that combination to the dibromide does not occur. At high temperatures it is probable that true bimolecular reaction might result.

This reaction is, however, readily catalysed by surfaces,[2] and it is found that " polar " surfaces are more effective than non-polar surfaces; thus, paraffin wax is, as shown by more recent unpublished experiments, quite inert as a catalyst, a water or ammonia film is more effective than cetyl alcohol, which, in turn, is somewhat less effective than stearic acid. Although it cannot be definitely stated on account of our lack of knowledge of the structure of the surfaces that " polar " groups possess different activities, it is clear that the " polar " groups are more effective than non-polar groups. This conception is an exemplification of the idea originally put forward by Armstrong[3] that chemical action is reversed electrolysis Whilst it is clear that the catalyst has lowered the critical energy increment necessary for the union of the gases, the hypothesis of Armstrong would lead us to anticipate that the structure of the ternary complex, gases-surface, at the moment of formation must be similar in electrical properties to a cell.

Our ideas of the electrical structure of complex organic molecules are at the present time undergoing rapid changes, and on such subjects as the transmission of " polarity ", the dissociation constants of organic acids, and the structure of double bonds, opinion is sharply divided.[4] The following considerations may be put forward as a somewhat general expression of method by which it is hoped that an adequate understanding both of the nature and stability of these catalytic complexes may be ultimately arrived at. The conception of the catalyst in these liquid reactions as a charged ion leads us to consider that it is not alone the kinetic impact of collision that effects disruption, but that, in addition to the energy supplied by kinetic agitation, which solvent molecules could supply equally well, an electric distortion of the molecule is produced simultaneously. Indeed, it would appear that this electrical distortion produced, or the electrical work done in approach, is a much more important factor than the kinetic factor. There are few catalytic homogeneous gas reactions, owing to the absence of electric effects The catalyst must thus form a transitory highly reactive chemical compound with the solvated reactant

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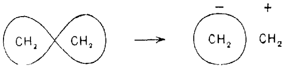
[1] Stewart and Edlund, *J. Amer Chem. Soc*, 1923, **45**, 1014.

[2] Stewart and Edlund, *J. Amer Chem Soc.*, 1923, **45**, 1014, Norrish, *J. Chem Soc.*, **1923**, **123**, 3006.

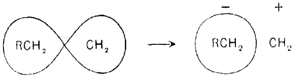
[3] *J. Chem. Soc.*, 1885, p. 39, *ibid*, 1893, p. 145.

[4] See *Trans. Farad. Soc*, 1923, for a résumé of the subject.

Saturation of a double bond. -Since the double bond in the ethylene molecule is broken when the dibromide is formed it is assumed by many, especially by Lowry, that activation consists in the breaking of a double bond to form a polar molecule CH_2-CH_2 On the assumption that the valency electron of the bond forms a binuclear orbit this process may be represented diagrammatically as follows

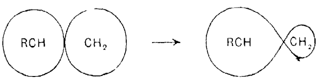


In the case of substituted unsymmetrical ethylene molecules we may represent the rupture on this point of view



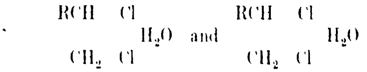
where R, the substituent group, renders the group RCH more electronegative than CH_2

It is found, however, on the addition of substances such as HBr, that two compounds are always formed, RCH_2 CH_2Br and $RCH\,Br$ CH_2, and for this reason it has been suggested that the excited or activated ethylene molecule is not necessarily " ionised ", but that the electron travels round the two nuclei in such a way that it remains for a longer time in the orbit of the RCH than of the CH_2 group a view which can be diagrammatically presented as follows



Thus the compound will be oscillating in " polarity " as the electron moves in its orbit round one focus to the other, but the RCH will exist for a longer time than the CH_2 and the chance of reaction by collision in this form thus more favourable As in the hydrogen chlorine combination, the halogen molecule is more easily excited in the presence of a polar molecule such as water Reaction thus ensues between the ethylene and the halogen through the agency of water, primarily by stabilising the active form of the halogen which reacts with the ethylene when in one of its polar forms

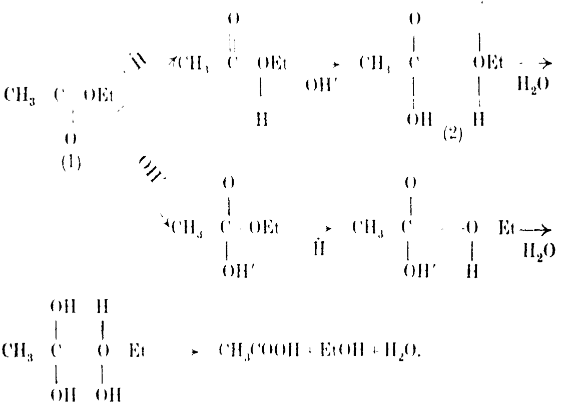
The activated complexes on this view would be represented diagrammatically as



$$\begin{matrix} RCH & Cl & \\ & & H_2O \\ CH_2 & Cl & \end{matrix} \quad \text{and} \quad \begin{matrix} RCH & Cl & \\ & & H_2O \\ CH_2 & Cl & \end{matrix}$$

Contrary to the original suggestion of ionising the double bond linkage, the catalyst merely assists in activating the halogen or halide, and by forming a complex with it which possesses a smaller energy of activation. This view could be put to experimental proof, for catalysts should not alter the ratio of the two products formed on the addition of halide acids to asymmetric substituted ethylene derivatives.

The hydrolysis of esters. Lowry[1] has developed, on the conception of ionisation of the double bond referred to above, a mechanism to interpret the hydrolysis of esters by hydrogen or hydroxyl ions. According to this view the action of these catalysts on the ester can be diagrammatically represented as follows:



$$\begin{matrix} & OH & H & \\ & | & | & \\ CH_3 & C & O & Et \\ & | & | & \\ & OH & OH & \end{matrix} \rightarrow CH_3COOH + EtOH + H_2O.$$

The function of the catalyst is to convert the closed form (1) of the ester into the amphoteric bipolar molecule (2) by (*a*) direct addition, first of the catalytic ion, (*b*) attraction of the ion of opposite sign, thus effecting the addition of the elements of water.

A slight modification of this view would be more in harmony with the ideas already referred to. We may regard equally well the process of solution of an ester in water in the absence of a catalyst as effecting the formation of a complex ester-water, according to the scheme

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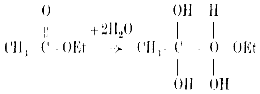
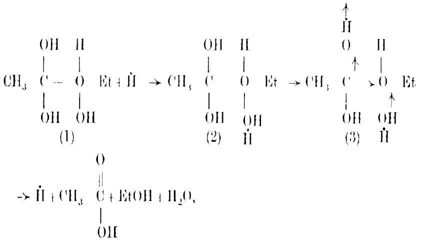
[1] Solvay Conference, 1925.



$$\mathrm{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OEt} \xrightarrow{+2\mathrm{H_2O}} \mathrm{CH_3{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle H}{|}}{O}}{-}OEt}$$

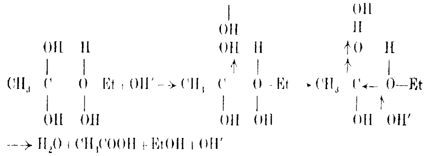
The unhydrated or less hydrated form of the catalytic hydrogen or hydroxyl ion can by impact, form an unstable complex which breaks down to acid and water and hydrogen ion again as follows



$$\underset{(1)}{\mathrm{CH_3{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle H}{|}}{O}}{-}Et}} + \dot{\mathrm{H}} \rightarrow \underset{(2)}{\mathrm{CH_3{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}\underset{\underset{\underset{\displaystyle \dot{H}}{\displaystyle OH}}{|}}{\overset{\overset{\displaystyle H}{|}}{O}}{-}Et}} \rightarrow \underset{(3)}{\mathrm{CH_3{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\overset{\overset{\uparrow}{\dot{H}}}{\displaystyle O}}{\uparrow}}{C}}{\succ}\underset{\underset{\underset{\displaystyle \dot{H}}{\displaystyle OH}}{\uparrow}}{\overset{\overset{\displaystyle H}{|}}{O}}{-}Et}}$$

$$\rightarrow \dot{\mathrm{H}} + \mathrm{CH_3{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O}{\|}}{C}}} + \mathrm{EtOH} + \mathrm{H_2O},$$

where the arrows in (3) indicate the passage of the electron effected by the collision of the stable molecule (1) with the highly active charged ion In a similar manner we may write



$$\mathrm{CH_3{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle H}{|}}{O}}{-}Et} + \mathrm{OH'} \rightarrow \mathrm{CH_3{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\overset{\overset{\displaystyle |}{OH}}{\displaystyle OH}}{\uparrow}}{C}}{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle H}{|}}{O}}{-}Et} \rightarrow \mathrm{CH_3{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\overset{\overset{\displaystyle OH}{H}}{\uparrow O}}{\uparrow}}{C}}{\leftarrow}\underset{\underset{\displaystyle OH'}{\uparrow}}{\overset{\overset{\displaystyle H}{|}}{O}}{-}Et}$$

$$\longrightarrow \mathrm{H_2O} + \mathrm{CH_3COOH} + \mathrm{EtOH} + \mathrm{OH'}$$

The catalytic activity of the two ions is, on this view, to be ascribed to the stable water-ester complex (1) being chemically reactive, the catalytic ion being attached at one point of the molecule and one being subsequently liberated at another point There is definite evidence for the rapid hydration of esters and sugars in aqueous solution, the magnitude of which is, however, no criterion of subsequent speed of hydrolysis or inversion and it is to this complex that the catalytic ion is added, another ion leaving the molecule at another point at the moment of decomposition. That esters may be regarded as amphoteric electrolytes capable of uniting with both hydrogen and hydroxyl ions was a view originally put forward by Euler (see Chapter XIII.), who has been able to measure both the acid and basic dissociation constants in a number of cases. Whilst Euler's investigations afford a clear argument why the formation of the complex ions from the ester with either of the catalytic ions of water occurs, the reason why these are particularly reactive can only be arrived at from speculations and considerations of the nature already discussed. Many other examples of attempts to formulate the mechanism of the reaction and to account for the instability of the complexes have been investigated in this way, such as the mutarotation of the sugars and the decomposition of the chloramines.

The most detailed examination of a case of homogeneous reaction in which anions exert a catalytic action has been made by Bronsted and Pedersen,[1] who investigated the catalytic decomposition of nitramide.

Nitramide decomposes in solution according to the reaction

$$H_2N_2O_2 \longrightarrow H_2O + N_2O;$$

the decomposition is strongly catalysed by anions which may here be represented as hydrogen ion acceptors and the mechanism of reaction depicted as follows:

$$H_2N_2O_2 + A' \longrightarrow (A'\dot{H}) + HN_2O_2' \longrightarrow OH' + N_2O.$$

In aqueous and in slightly acid solution nitramide undergoes a slight decomposition which is unaffected by the nature or strength of the acid present; this spontaneous decomposition may be regarded as a measure of the basicity of the water with which the nitramide reacts, according to the reaction

$$H_2N_2O_2 + H_2O \longrightarrow H_3O + HNO_2' \longrightarrow H_3O + OH' + N_2O.$$

If the concentration of the nitramide be x the reaction velocity in aqueous solution will be

$$\frac{dx}{dt} = kx.$$

In the presence of a catalyst of concentration c we obtain

$$\frac{dx}{dt} = kx + k'cx,$$

or by

$$\frac{x}{x_0} = \{k + k'c\}t$$

In aqueous solution it is found to be ·000385 at 15° C. with a half life of 13·2 hours.

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[1] *Zeitsch. physikal. Chem.*, 1924, **108**, 185.

Bronsted and Pedersen have examined the catalytic activity of the anions of a number of organic acids by determining the rate of reaction in the presence of their salts, together with sufficient acid to prevent the formation of hydroxyl ions by hydrolysis of the salt In the following table are given the catalytic activity of the anions investigated, together with the dissociation constants of the acids It is interesting to note an empirical relationship between these two properties

Acid	Dissociation Constant K	Velocity Constant k	$k/K^{0.83}$
Propionic	$1.34 \times 10^{[illegible]}$	0.65	$5.9 \times 10^{[illegible]}$
Acetic	1.8×10^{-5}	0.50	5.8
Phenylacetic	5.3×10^{-5}	0.23	6.5
Benzoic	6.5×10^{-5}	0.19	6.3
Formic	2.1×10^{-4}	0.082	7.2
Salicylic	1.0×10^{-3}	0.021	6.2
Dichloracetic	5.0×10^{-2}	0.0007	5.8
		Mean	$6.2 \times 10^{[illegible]}$

They have also extended their investigations to the anions of the polybasic acids Thus, in the case of salts of dibasic acids there are present in solution two anions governed by the equilibria

$$H_2X \rightleftarrows \dot{H} + HX' \quad k_1$$

$$HX' \rightleftarrows X'' + H \quad k_2$$

the velocity of decomposition is accordingly given by the expression

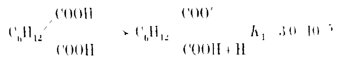
$$\log \frac{t}{t_0} = (k + k_1c_1 + k_2c_2)t,$$

where k' and k'' are the catalytic constants of the anions HX' and X'' respectively

The results obtained were exceedingly interesting in the light of the probability of dissociation in the two stages

If we compare the dissociation of the two acids, caprylic and suberic,

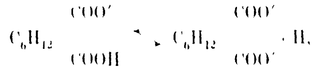
$$C_7H_{15}COOH \rightarrow C_7H_{15}COO' + \dot{H} \qquad K = 1.44 \times 10^{-5}$$



$$C_6H_{12}\begin{matrix} COOH \\ COOH \end{matrix} \rightarrow C_6H_{12}\begin{matrix} COO' \\ COOH + H \end{matrix} \qquad K_1 = 3.0 \times 10^{-5}$$

we may regard the resultant dissociation constants which stand in the ratio of 1 : 2 from a purely statistical point of view We can assume that the organic ions of each acid are equally hydrophilic in character, the probability of each acid losing a hydrogen ion from one carboxyl group and its recombination being equal The dibasic acid, however can lose a hydrogen ion from either carboxyl group, but combination can only occur with the group which has lost the ion; in consequence, we might anticipate that the dissociation constant which represents the ratio of the speeds of dissociation and recombination would be twice as great for the dibasic acid as for the monobasic acid, a conclusion justified by the experimental data. If we now compare the monobasic acid with the dissociation of the dibasic acid in its second stage,

$$C_7H_{15}COOH \rightleftarrows C_7H_{15}COO' + \dot{H}$$



$$C_6H_{12}\begin{matrix}COO'\\ COOH\end{matrix} \rightleftarrows C_6H_{12}\begin{matrix}COO'\\ COO'\end{matrix} + \dot{H},$$

and again assume the two ions to be equally hydrophilic in character, it is clear that the probability of dissociation for each acid is identical, but the chance of recombination is twice as great for the dibasic acid as for the monobasic acid. We thus obtain what may be termed a statistical factor regulating the degree of dissociation of polybasic acids in which the anions are equally hydrophilic. These factors are shown in the following table:

Dissociation	Statistical Factor n
$HQ \rightleftarrows \dot{H} + Q$	1
$H_2Q \rightleftarrows HQ' + \dot{H}$	½
$HQ' \rightleftarrows Q'' + \dot{H}$	2
$PH_3 \rightleftarrows PH_2' + \dot{H}$	⅓
$PH_2' \rightleftarrows PH'' + \dot{H}$	1
$PH'' \rightleftarrows P''' + \dot{H}$	3

In the light of these considerations the data of Bronsted and Pedersen for dibasic acids and the tribasic phosphoric acid show a remarkable uniformity, as is clear from the following table:

Acid	K_1	n	k	$k\,(nK_1)^{0\cdot83}$	K_2	n	k	$k\,(nK_2)^{0\cdot83}$
Phosphoric	$8{\cdot}9 \times 10^{-3}$	⅓	0·0079	$6{\cdot}3 \times 10^{-5}$	$4{\cdot}9 \times 10^{-8}$	1	86	$7{\cdot}2 \times 10^{-5}$
Tartaric	$9{\cdot}7 \times 10^{-4}$	½	0·0363	$6{\cdot}3 \times 10^{-5}$	$3{\cdot}7 \times 10^{-5}$	2	0·165	$6{\cdot}2 \times 10^{-5}$
Succinic	$6{\cdot}5 \times 10^{-5}$	½	0·320	$6{\cdot}0 \times 10^{-5}$	$2{\cdot}1 \times 10^{-6}$	1	1·86	$6{\cdot}2 \times 10^{-5}$
Malic	$4{\cdot}0 \times 10^{-4}$	½	0·0765	$6{\cdot}4 \times 10^{-5}$	$6{\cdot}9 \times 10^{-6}$	2	0·72	$6{\cdot}8 \times 10^{-5}$
				Mean value $6{\cdot}2 \times 10^{-5}$				Mean value $6{\cdot}4 \times 10^{-5}$

It is clear that the catalytic decomposition of nitramide in the presence of the salts of various polybasic acids permits us to obtain information on the statistical factors of these acids as well as their dissociation constants. For the dissociation of non-symmetrical dibasic acids, the effect of asymmetry on the statistical factor might be determined from experimental values of k'', the catalytic constant of the dibasic anion, and the value $6{\cdot}2 \cdot 10^{-5}$ of the constant $k''(nK_2)^{0{\cdot}83}$.

The method permits of several interesting applications. Thus, they have investigated a typical pseudo-acid in the form of nitrourethane which, as shown by Hantzsch,[1] can exist in two forms

$$\underset{\text{Isonitrourethane}}{NO_2 . NH . COOC_2H_5} \rightleftarrows \underset{\text{Nitrourethane}}{C_2H_5OOC - N = N . OOH}$$

The acid form can undergo dissociation yielding a catalytic anion $C_2H_5OOC . N . NOO'$, which was found to yield a catalytic constant of $0{\cdot}0066$. From conductivity data the dissociation constant K is found to be $1{\cdot}3 \cdot 10^{-4}$,[2] whence the constant $kK^{0{\cdot}83}$ is found to be $1{\cdot}08 \cdot 10^{-5}$ or some six times smaller than the value obtained for the other acids. It must be concluded that the true strength of the acid nitrourethane is some eight times greater than the value observed with the pseudo acid in solution.

Again, since the decomposition rate of nitramide is dependent on the presence of hydrion acceptors in the solution, all substances which function as bases in this sense are catalytically active. We have already noted that water may be regarded as a base in that it can accept hydrogen ions and does in fact possess a small catalytic activity.

The catalytic activity constant of aniline was found to be $k = 0{\cdot}531$. Bronsted and Pedersen point out that the value of the dissociation constant of the ion

$$C_6H_5NH_2\dot{H} \rightleftarrows C_6H_5NH_2 + \dot{H} \quad K = 2{\cdot}0 \cdot 10^{-5}$$

is very close to that of acetic acid,

$$CH_3COOH \rightleftarrows CH_3COO' + \dot{H} \quad K = 1{\cdot}8 \cdot 10^{-5},$$

and, as will be noted, the specific catalytic activities are almost identical. The values for many hydrogen ion acceptors are shown in the following table:

	K	k
Water	?	0·00038
Aniline	$2{\cdot}0 \cdot 10^{-5}$	0·531
Quinoline	$1{\cdot}2 \cdot 10^{-5}$	1·9
Dimethylaniline	$6{\cdot}3 \cdot 10^{-6}$	2·7
Pyridine	$4{\cdot}4 \cdot 10^{-6}$	4·6

The effect of neutral salts in increasing the ionic activity is well exemplified in the case of the addition of potassium nitrate to propionic acid, in which the following data were obtained:

C_{PH}	0·101	0·101	0·101	0·101
C_{KNO_3}	0	0·02	0·05	0·1
$k \cdot 10^5$	114	125	128	132
$\{k - k_{H_2O}\} \cdot 10^5$	76	87	90	94
$C_{P'} \cdot 10^3$	1·17	1·34	1·38	1·44
$K \cdot 10^5$	1·37	1·80	1·90	2·07

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[1] *Ber.*, 1899, **32**, 575, 3066.

[2] Bauer, *Zeitsch. physikal. Chem.*, 1897, **23**, 409.

CHAPTER IV

THE THEORY OF HETEROGENEOUS CATALYTIC REACTIONS

HETEROGENEOUS catalytic reactions are those that take place at surfaces. Whilst many examples of reactions are known which occur either at solid-gas or solid-liquid interfaces, but few cases of catalytic reactions at liquid-gas interfaces have been established with certainty, although Rideal and Wolf[1] have examined the destruction of rennin at an air-liquid interface, and Norrish and Rideal[2] the catalytic influence of oxygen at a liquid sulphur hydrogen interface. There is, however, little reason to doubt that the specific effects due to the properties inherent at all interfaces will have their influence on reactions taking place at liquid surfaces.

Of fundamental importance in the theory of the mechanism of heterogeneous catalytic actions is the existence of an interfacial surface energy. In the case of liquid-gas or liquid-liquid interfaces the free surface energy σ is readily determined by various experimental methods, and from a knowledge of this value as well as the temperature coefficient of the surface energy $\frac{d\sigma}{dT}$ the total surface energy u may be calculated with the aid of the Gibbs-Helmholtz equation

$$\sigma - u = T\frac{d\sigma}{dT}$$

We must postulate the existence at the interface solid-gas or solid-liquid of a similar surface energy, although, owing to the immobility of one phase, its value cannot readily be determined. The existence of such a surface energy in solids is in fact confirmed by the phenomenon of cohesion, for, on cutting a crystal, two surfaces are formed in which the previously locked cohesive forces are now unsaturated. In general, the surface atoms of a solid are situated unsymmetrically to the forces of cohesion as compared with the internal ones. Attempts have been made to compute the surface energy of solids by indirect methods. On the supposed analogy between small crystals and small drops, the increase in solubility of a crystal as a reciprocal function of its radius has been utilised for this purpose. Although the analogy may be criticised, the magnitudes of the values obtained are by no means unreasonable.

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[1] *Proc. Roy. Soc.*, 1924, **97**A, 106.

[2] *J. Chem. Soc.*, 1923, **123**, 696; 1924, **125**, 1689, 3203, 2070.

Since, in systems not in equilibrium, reactions may proceed associated with a decrease in free energy, if adsorption (at an interface) of constituents present in a fluid bulk phase is associated with a decrease in the free surface energy, such a reaction will ensue. We shall have occasion to note that this property of adsorption is common *to all interfaces, that at liquid interfaces the magnitude of the effect depends only on the properties of the system, but at solid surfaces the physical structure as well as the chemical properties of the surface have to be taken into consideration.*

Adsorption at liquid interfaces.—On the addition of a solute to a liquid a change in the surface energy of the liquid occurs. If the added solute has the effect of diminishing the surface energy, the concentration of the solute in the surface film will be greater than that in the bulk of the liquid. The quantitative relationship between the excess concentration of the surface film over the bulk of the solution and the lowering of the surface tension has been developed by W. Gibbs and Sir J. J. Thomson. In its simplest form we may express this relationship as follows

$$\Gamma = -\frac{d\sigma}{df}$$

where Γ is the excess surface concentration in grm.-mols. per sq. cm.,
σ the surface tension,
f the chemical potential of the solute.

If the solute obeys the laws of ideal solution, then

$$f = f_0 + RT \log c,^1$$

whence $$\Gamma = -\frac{1}{RT}\frac{d\sigma}{d \log c} = -\frac{c}{RT}\frac{d\sigma}{dc}$$

Similarly for those cases in which the solute elevates the surface tension of the liquid there will be a smaller concentration of solute in the surface film than in the bulk of the liquid.

We are thus in a position to calculate the composition of the surface film, frequently termed the Gibbs layer. We have not, however, made any assumptions as to the thickness of the film in which the forces of surface tension produce a modification in chemical composition. We shall have occasion to observe that the investigations of Lord Rayleigh, Langmuir, Devaux, Labrouste and N. K. Adam on the effect of insoluble fatty acids and their derivatives on the surface tension of water, make it practically certain that these substances

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[1] For non ideal solutions $f = f_0 + RT \log a$ or $f_0 + RT \log \gamma c$ where γ is the activity coefficient and a the thermodynamic activity.

spread over a water surface in a unimolecular layer. For soluble substances, direct evidence for the unimolecular character of the Gibbs layer is not forthcoming, but it may be concluded that in many cases such an assumption is justified. The evidence for this assumption is twofold. In the first case, as pointed out by Langmuir, if it be assumed that the Gibbs layer is unimolecular in character the limiting areas per molecule for organic substances, which are adsorbed at the interface, calculated with the aid of the Gibbs equation, are in good agreement with the areas anticipated from other considerations. Again, if molecules of the solute are positively adsorbed at the interface we may regard the lowering of the surface tension of the pure solvent by the solute $F = \sigma_0 - \sigma_{\text{solution}}$ as being due to the kinetic agitation of the adsorbed solute molecules on the surface, thus F will be analogous to a two-dimensional osmotic or gas pressure. This suggestion, originally put forward by Traube, was rejected by later investigators, notably by Milner and V. Szyskowski, for the law $F.A = RT$, the two-dimensional equivalent to the three-dimensional law $PV = RT$, was found not to express the observed relationship between F and A, where F is defined as above and A as $\frac{1}{\Gamma}$.

A more careful examination of the state of this two-dimensional solution, however, by Schofield and Rideal[1] has indicated that the surface solutions are always relatively concentrated and may be regarded as equivalent to gases at high pressures or to strong solutions. The two-dimensional analogue of Amagat's equation of state,

$$F(A - B) = xRT,$$

where B is the limiting area and $\frac{1}{x}$ the coefficient of association, is found to agree with the experimental data, and the $F.A$ curves of solutions of fatty acids and esters are found to reproduce to a surprising degree of accuracy the PV curves for gases such as nitrogen and ethylene.

Whilst on surfaces of most liquids the Gibbs layer is but unimolecular in thickness, it cannot be said that the adsorbed solute possesses all the properties of the pure solute in bulk. Thus, saturation of the Gibbs layer in the case of ethyl alcohol-water mixtures occurs at a concentration of 0·3 molar, yet the surface phase, although consisting of pure ethyl alcohol, is by no means identical in properties with a free surface of ethyl alcohol. Even more definite in this direction are the experiments of Iredale[2] on the adsorption of vapours on the surface of mercury. Whilst the surface tension of mercury is lowered very markedly by the adsorption of a unimolecular layer of vapour such as ethyl acetate, benzene, or water, and the lowering is more pronounced he more closely packed the unimolecular film on the surface, yet he vapour pressure of even a closely packed unimolecular film is less han that over the pure liquefied vapour at the same temperature.

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[1] *Proc. Roy. Soc.*, 1925, **107**A, 57.

[2] *Phil. Mag.*, 1923, **45**, 1099; **48**, 165, 1727

From these and Iredale's experiments we may conclude that the uilding up of the primary Gibbs layer is associated with a marked hange in the surface energy of the liquid adsorbent, and that the uilding up of the secondary films or diffuse layer is associated with a urther definite but very much smaller decrease in free energy

In dealing with the adsorption of vapours and liquids by solids, e shall again have occasion to note that the formation of what may e termed the primary film, unimolecular in character, is associated ith large thermal effects, but that in many cases secondary film ormation, which may be multimolecular in thickness, also takes place.

Evidence for molecular orientation in adsorption at liquid surfaces. – *The work commenced by the late Lord Rayleigh* [1] *and developed* by Hardy,[2] Marcelin,[3] Langmuir,[4] Labrouste,[5] Harkins,[6] N K Adam,[7] and others, on the surface tension of solutions has given us a deeper insight into the mechanism of adsorption, the bearing of which on catalytic processes is of fundamental importance

If we bring two liquid surfaces together of surface tensions σ_A, σ_B to form an interface of surface tension σ_{AB} there will be a certain decrease in the free energy of the system given by the expression

$$W = \sigma_A + \sigma_B - \sigma_{AB}$$

In the following table are summarised some of the values for this decrease in free energy when various liquids are brought into contact with water and mercury

Substance	W with Water	W with Mercury
	Ergs per sq cm	Ergs per sq cm
Pentane	18 9	
Hexane	20·6	60 8
Octane	21·6	65 5
CCl_4	24 0	74·8
Water	73	91 5
Ethyl iodide		110
Methyl iodide		110
Carbon disulphide	21	90
Ethyl ether	39 9	
Alcohols	47·8 51 8	
Organic acids	46 50	
Ethyl esters	37-46	

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[1] *Proc Roy Soc* 1890, **47**, 281, *Phil Mag* 1899, **48** 331

[2] *Proc Nat Acad Sci*, 1917, **3**, 141, *Proc Roy Soc*, 1912, **86** 610; 1913 **8** 313

[3] *J de Physique*, 1914, **1** 19

[4] *J Amer Chem. Soc*, 1917, **39**, 186

[5] *Ann d Phys* 1920, **14**, 164

[6] *J. Amer Chem Soc*, 1917, **39**, 354

[7] *Proc Roy Soc*, 1921, **99A**, 336, 1922, **101**, 452, 1922 **101**, 517, 1923, **103**, 677.

It is evident that the decrease in free energy when a liquid is brought into contact with water or mercury is most marked when the former contains certain reactive groupings such as the halide, sulphide, and hydroxyl for mercury, and the hydroxyl, oxonium, and carboxyl for water.

The decrease in free energy is the result of the action of the adsorption forces between the surface layers of the two liquids, and it is evident that these adsorptive forces operate on a specially reactive part of the molecule. Thus in the case of fatty acids floating upon the surface of water we should anticipate that the acid would be anchored to the water by means of the carboxyl group, since the hydrocarbon chain possesses but little adhesion for water.

Direct confirmation of this hypothesis has been obtained by measurement of the surface tension of water to which definite amounts of the highly insoluble long-chain fatty acids, alcohols, and substituted ureas dissolved in benzene have been added. If a definite quantity of fatty acid, *e.g.* palmitic acid, be dissolved in benzene and dropped upon the surface of water, after the evaporation of the benzene the water will be covered with a layer of palmitic acid and the surface tension of the water will be lowered. If the lowering of the surface tension be plotted against the area of the water covered with this amount of palmitic acid, a curve of the following form will be obtained.

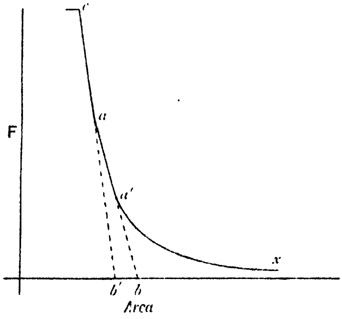


FIG. 2

It will be noted that the curve is divisible into three parts, a linear portion *ca*, a second linear portion *aa'*, and a curved portion *a'x*. The explanation of the curve obtained is readily understood from the following arguments.

If a small quantity of fatty acid be allowed to expand over a wide area of water the *F. A* relationship will be defined by some point on the curve in the region *a'x*. On contracting the area the force, *i.e.*

the apparent lowering of the surface tension, increases but slowly until, at the point *a'*, it rises rapidly in a linear manner. At the point *a*, under higher compressions, there is a break in the curve, which proceeds again in a linear manner to the point *c*, where an abrupt change in the surface tension is noted.

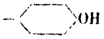
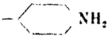
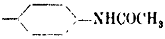
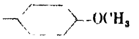
From a knowledge of the number of molecules of fatty acid placed on the measured area of water, the mean area per molecule on the assumption of a unimolecular film corresponding to the pressures *a'* and *a* can readily be determined. The prolongation of the *ca* curve to *b'* gives us as the area per molecule *ob'* 21 Å, of *ob* 25·2 Å. The interesting points in connection with these measurements are, firstly, that, on the assumption that the density of palmitic acid in the thin film is identical with that in the bulk, the covering power of the fatty acid, from our knowledge of the approximate sizes of the molecules, confirms our previous hypothesis of a unimolecular layer of fatty acid molecules on the surface of the water. The second point of interest is that if similar curves for other long-chain fatty acids be made, the areas per molecule corresponding to the pressures at *a* and *a'*, *i.e.* at the breaks in the curve, are identical with those of palmitic acid, as is exemplified in the following data of N. K. Adam.

Acid	*ob'* in Å	*ob* in Å
Myristic	21·0	25·1
Pentadecylic	21·0	25·1
Stearic	21·0	25·1
Behenic	21·0	25·1

All these carbon chain acids have a different number of carbon atoms in their chain, yet, under corresponding compressions in a surface film occupy identical areas. We can thus conclude (Langmuir) that all the molecules of each acid, under these compressions at any rate, are orientated in a vertical plane to the water surface and thus present equal cross-sectional areas to the lateral compressional force.

On this assumption of a vertical orientation of the molecules we must account for the fact that the molecule of the fatty acid apparently possesses two parts of different area under zero compression *ob'* = 21 Å, *ob* = 25 Å, possessing different compressibilities. These, as N. K. Adam has pointed out, correspond to the hydrocarbon chain *ob'* and the carboxyl head *ob'*. The area *ob'* of 21 Å should thus be a measure of the cross-section of a hydrocarbon chain. Now the molecular volume $V_{CH_2} = 17{\cdot}8$ c.c. at the m.p. and the distance between the carbon atoms in a diamond is 1·52 Å, hence the area of a CH_2 group is *ca.* $\frac{17{\cdot}8}{N\ 1{\cdot}52\ 10^{-8}} = 19{\cdot}3$ Å, in fair agreement with the observed value.

If the area 25·2 Å corresponds to that of the carboxyl head immersed in the water, the replacement of this head to the molecule by other groups should give different values to *ob*. Some of N. K. Adam's values for the areas of various heads are given below.

Head Group.	Area in Å.U.
$-COOH$	25·1
$-C{=}CH.COOH$	28·7
$-NH-CO-NH_2$	26·3
$-CONH_2$	21·5
$-COOC_2H_5$	22·3
$-CH_2OH$	21·7
$-CH_2CN$	27·5
	23·8
	23·7
	28·2 below 24° 25·8 above 29°
	23·8

These conclusions, based on the study of films of relatively insoluble organic compounds on the surface of water, which have been amply confirmed and extended in various directions, go far to substantiate

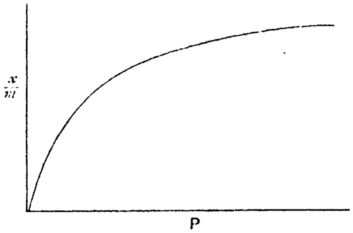


FIG. 3

the statement that the molecules in the Gibbs film are definitely orientated and attached to the adsorbing agent by a specific (or more than one) point of attachment [1]

Adsorption at solid interfaces.—The adsorption or surface saturation of a solid by a gas or vapour is frequently complicated by processes of solution to form either a solid solution or an actual chemical compound with the adsorbate. Again, in the case of many porous materials, the pores or capillaries of the solid, when of small diameter, offer a by no means negligible resistance to the flow of gas, in consequence of which penetration may proceed for prolonged periods of time.

As has already been indicated, owing to the existence of a surface energy in solids, we should anticipate, on analogy with liquid interfaces, the adsorption of gases or vapours if attended with a diminution of the free surface energy of the surface In addition, substances possessing a high specific surface and a concomitant surface energy, such as charcoal, will be valuable adsorbing agents

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[1] It may be noted that the polar head of a film on a water surface is not necessarily attached to only one water molecule. From a study of gel formation it appears more than probable that a cluster of water molecules are attached to the "hydrated" polar head.

The general asymptotic form of curve connecting gas or vapour pressure p with the amount adsorbed x, per m grms of adsorbate, is shown on p 65

Many attempts have been made to express these curves in mathematical form and to interpret the mechanism of such adsorption, accurate data on the adsorption of gases by charcoal being available[1] As a good approximation the equation of Freundlich may be applied to the experimental data

Freundlich's isotherm equation may be expressed in the form

$$\frac{x}{m} = ap^{\frac{1}{n}},$$

or

$$\log\frac{x}{m} = a + \frac{1}{n}\log p,$$

where x is the amount adsorbed by m grms of material under a partial pressure p, a and n being constants

The value of n varies markedly, not only with the nature of the gas but also with the composition of the adsorbent as is exemplified by the following figures for adsorption of gases at 20° C

Gas	$\frac{1}{n}$ Charcoal	$\frac{1}{n}$ Glass
CO_2	0 394	0 66
NH_3	0 437	0 53
SO_2	0 324	0 28
$CHCl_3$	0 122	
N_2O		0 49

The two constants a and n also vary with the temperature, and it is significant to note that n approaches unity on elevation of the temperature or for low gas pressures Thus, Chappuis[2] obtained a value of $\frac{1}{n} = 0\ 81$ for the adsorption of ammonia by charcoal between 3 and 5 millimetres of mercury, whilst Travers[3] gives the following data for the adsorption of carbon dioxide by charcoal

Temp °C	a	$\frac{1}{n}$
-78	14 29	0 133
0	2 96	0 333
35	1 236	0 461
61	0 721	0 477
100	0 324	0 518

The Freundlich isotherm leads us to the conclusion that a definite area of adsorbing surface may adsorb an indefinitely large amount of gas, provided that the pressure is sufficiently high. This conclusion is not justified by experiment, as a definite saturation value. frequently well defined has been found to exist in a great number of cases. Arrhenius[1] and Schmidt[2] were the first to introduce the concept of a definite saturation value for the case of an adsorbent exposed to a gas, the equation developed.

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[1] Vater, *Zeitsch f Elektrochem*, 1912, **18** 724 Travers, *Proc Roy Soc*, 1915, **78A**, **9**; Homfray, *Zeitsch physikal Chem*, 1910, **71**, 139, 687, Titoff, *ibid*, 1910, **74**, 641, Geddes, *Drude's Ann*, 1909, **29**, 197, Richardson, *J Amer Chem Soc*, 1917 **38**, 1818

[2] *Wied Ann*, 1883, **19**, 29

[3] *Loc cit*

$$\log_{10}\frac{S}{S-x} - 0{\cdot}434\frac{x}{S} = \frac{p}{K},$$

containing two constants, S the saturation value and K, an equation which is likewise valid over a fairly wide range of pressures.[3] The values of S for charcoal for various gases is somewhat significant.

Gas	S c.c. at N.T.P. per grm.	Gas	S c.c. at N.T.P. per grm.
NH_3 . .	158	CO_2	60
C_2H_4 . .	58	O_2	87
CO .	116	N_2 .	90
CH_4 .	91	Ar .	87

Langmuir[4] also arrived at the conclusion that the Freundlich isotherm does not represent the adsorption pressure relationship to any degree of accuracy. As has already been indicated, the surface of a solid may be regarded as an adsorbing lattice-work of atoms. If definitely crystalline, the number of such adsorbing centres may be computed from the atomic diameters, whilst if the surface be irregularly crystalline or amorphous, the number of these elementary spaces per square centimetre cannot be determined directly.

We may regard adsorption as the result of an equilibrium arrived at between two definite and distinct processes, condensation and evaporation. If a gas molecule or atom strikes an empty space on the adsorbing surface it condenses and is held there for a period of time. It is here subject to molecular collisions, and the kinetic energy of translation will in time reach such a value that it is capable of breaking away from the surface again and evaporating. In considering a number of such condensed molecules or atoms we are evidently justified in speaking of the average life of an atom on the surface (τ), which may vary from a small fraction of a second in cases where the adsorbing forces are small and the temperature high to almost indefinite periods where the conditions are favourable, as is exemplified in the following data[5] for the adsorption of carbon monoxide on platinum.

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[1] *Nobel Inst.*, 1911, **2**, 7.

[2] *Zeitsch. physikal. Chem.*, 1912, **78**, 607.

[3] See also Williams, *Proc. Roy. Soc. Edinburgh*, 1919, 287.

[4] *Phys. Rev.*, 1916, **8**, 149; *Proc. Nat. Acad. Sci.*, 1917, **3**, 141; *J. Amer. Chem. Soc.*, 1918, **40**, 1360.

[5] Langmuir, *Trans. Farad. Soc.*, 1922, **17**, 642.

Temp. °K.	Average Life in Seconds.
1000	0·00001
900	0·00004
800	0·00038
700	0·0066
600	0·30
500	63
450	2100
400	$1{\cdot}9\ 10^{5}$
350	$5{\cdot}8\ 10^{7}$
300	$1{\cdot}2\ 10^{11}$

From a series of experiments it was established that the number of molecules reflected without condensation and re-evaporation was small, as exemplified in the following table,[1] in which the accommodation factor (a) or the fraction condensed and then evaporated is given:

Gas	Surface	(a)
H_2	Smooth Pt	0·36
CO_2	,,	0·87
H_2	Pt black	0·71
CO_2	,,	0·98

We may thus regard all molecules hitting the surface as condensing there. The rate at which a gas at a pressure p will condense on a square centimetre of condensing surface may be determined with the aid of the well-known effusion equation of Herz and Knudsen:

$$\mu = 43{\cdot}75\ 10^{-6}\ \frac{p}{\sqrt{MT}},$$

where μ is the number of grm.-molecules striking per sq. cm. per sec.,
p the pressure in bars (10^6 bars = 1 atmosphere),
M the molecular weight of the gas,
T the absolute temperature.

At equilibrium we must consider a definite fraction of the surface covered with adsorbed gas θ', and a definite fraction bare, θ, then we have

$$\theta + \theta' = 1. \qquad . \qquad . \qquad (1)$$

The rate of condensation on the uncovered portion θ is $\alpha\mu\theta$, where α is the coefficient of accommodation, which is in general nearly unity.

The rate of evaporation from the covered area θ' can be written $\nu\theta'$, where ν is the rate of evaporation per square centimetre. At equilibrium the rates of condensation and evaporation must be equal, or

$$\alpha\mu\theta = \nu\theta', \qquad . \qquad . \qquad (2)$$

whence

$$\theta' = \frac{\alpha\mu}{\nu + \alpha\mu}. \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

If we put

$$\frac{\alpha}{\nu} = \sigma,$$

then

$$\theta' = \frac{\sigma\mu}{1 + \sigma\mu}$$

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[1] Knudsen, *Ann. Physik*, 1911, **34**, 593; Soddy and Berry, *Proc. Roy. Soc.*, 1911, **84**, 576.

If x grm.-mols. are adsorbed per unit area, the number of elementary spaces occupied will be $\frac{Nx}{N_o}$, where N is the Avrogadro number $= 6{\cdot}065\ 10^{23}$ molecules per grm.-mol. and N_o the number of elementary spaces per square centimetre. Whence

$$\frac{Nx}{N_o} = \theta' = \frac{\sigma\mu}{1+\sigma\mu},$$

whence

$$x = \frac{abp}{1+ap},$$

a and b being constants, or

$$\frac{p}{x} = \frac{1}{ab} + \frac{p}{b},$$

being Langmuir's equation for the adsorption isotherm. At low pressures $\sigma\mu$ will be small compared with unity. Hence

$$x = abp,$$

or the amount adsorbed will be proportional to the pressure. The amount adsorbed decreases rapidly with the temperature, since the rate of evaporation varies rapidly with the temperature.

At high pressures $\sigma\mu$ is large compared with unity, or

$$x = b.$$

We thus obtain a saturation value for the amount adsorbed. Saturation according to Langmuir's hypothesis is evidently obtained when the surface of the adsorbent is covered with a layer of the gas one molecule thick. Langmuir, in support of this hypothesis that saturation is obtained with a unimolecular layer, measured the adsorption of various gases on mica and platinum at low pressures. In the cases examined, with the exception of carbon monoxide on platinum surface, saturation was obtained with less than a unimolecular film, and the form of the p, x curve could be expressed with the aid of the equation given above. The best experimental evidence of saturated surfaces has been obtained in the study of adsorption of gases by catalytic agents. The adsorption of hydrogen by nickel, studied by Gauger and Taylor,[1] of hydrogen and carbon monoxide on copper by Pease,[2] and Hurst and Rideal,[3] of hydrogen and carbon monoxide on platinised asbestos as determined by Pollard,[4] all show saturation of the surface at pressures markedly less than 1 atmosphere at ordinary temperatures. Taylor[5] has shown that this ready attainment of saturation is consistent with the high heats of adsorption of these gases by the metallic catalysts. The experimental data also lead to interesting conclusions concerning the

[1] *J. Amer. Chem. Soc.*, 1923, **45**, 720.
[2] *Ibid.*, 1923, **45**, 1193, 2297.
[3] *J. Chem. Soc.*, 1924, **125**, 685, 694.
[4] *J. Phys. Chem.*, 1923, **27**, 365.
[5] 3rd Report on Cont. Cat., *J. Phys. Chem.*, 1924, **28**, 931.

surface of the catalyst, which are discussed in detail in a subsequent section.

The premises on which the various adsorption isotherm equations have been developed are different. In those of Freundlich and Arrhenius we tacitly assume that adsorption is a process akin to surface condensation, resulting in the formation of an atmosphere of condensed vapour and even liquid around the adsorbing material, the adsorbed film density decreasing presumably exponentially as we proceed from the surface until it is identical with the circumambient vapour. Langmuir assumes as a premise that the range of molecular action is limited to one molecule in thickness, and that the film is in consequence but one molecule thick.

Direct confirmation of either hypothesis in the case of charcoal is scarcely possible, owing to the uncertainty in the evaluation of the specific surface. Many measurements, however, have been made for the adsorption of vapours, *e.g.* water, benzene, chloroform, on the surfaces of glass, sand, quartz, and some metals, and in these cases the multimolecular nature of the adsorbed film has been substantiated.[1] The direct experimental evidence for the amount of gas adsorbed is thus by no means conclusively in favour of the general application of Langmuir's hypothesis.

We may, as Langmuir has suggested, attempt to avoid this difficulty by assuming that in those cases where a multimolecular film is apparently obtained we are in error in our computation of the actual area of the adsorbing material, *i.e.* fissures and capillaries are present in the material, or actual solution of the gas in the adsorbent has taken place; or again, we may consider that multimolecular films may actually exist for certain gases, especially vapours, in the presence of powerful adsorbing agents. In support of this second hypothesis indirect experimental evidence can be advanced from data on the heat of adsorption. For adsorption in multimolecular layers the heat of adsorption falls steadily with increasing quantities of gas adsorbed to a value sensibly equal to the heat of liquefaction.

Thus we note the data of Chappuis on the heat of adsorption of ammonia by meerschaum:

Pressure Range *in* cm. Hg.	*Q* cals. per grm.-mol.
0	20,500
0–0.5	12,700
0.5–3.7	11,300
2.9–21	8,970
21–57	7,600

Latent heat of liquefaction L = 5000.

The data of Lamb and Coolidge[2] on the heat of adsorption of vapours of many substances by charcoal in an ice calorimeter show likewise that the heat evolution per grm. of charcoal q was a logarithm function of the amount adsorbed x:

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[1] Langmuir, *Trans. Amer. Inst. Elect. Eng.*, 1921, **32**; Briggs, *J. Phys. Chem.*, 1905, **9**, 617; Katz, *Proc. Amst. Akad.*, 1912, **15**, 445; Pettijohn, *J. Amer. Chem. Soc.*, 1919, **41**, 447; Evans and George, *Proc. Roy. Soc.*, 1923, **103**A, 191.

[2] *J. Amer. Chem. Soc.*, 1920, **42**, 1146.

$$\log q = n + b \log x,$$

and a direct proportionality was not found, as would be the case if a unimolecular layer only was formed.

They likewise indicate a close connection between the heat of liquefaction and the heat of adsorption; whilst the close connection between the amount of gas adsorbed by charcoal and the cohesion of the gas as determined by the a term of Van der Waals' equation, lends additional support to the multimolecular layer hypothesis.

Gas	$a\ 10^3$	Adsorbed c.c. per grm. of Charcoal at Standard Pressure
He . .	0·42	0·227
Ar . . .	2·59	1·67
N_2	2·08	2·35
O_2 .	2·69	2·50
CO .	2·80	3·20
CH_4 . .	3·67	9·4
CO_2 .	7·01	30·4
NH_3 . . .	8·08	73
C_2H_4 .	8·83	41

Langmuir[1] in his investigations on the adsorption of carbon monoxide on platinum found that the adsorption isotherm for this gas could not be expressed in the form

$$x = \frac{abp}{1 + ap},$$

but in the form

$$x = b + \frac{ab'p}{1 + ap},$$

which can most readily be interpreted on the hypothesis that carbon monoxide is very strongly adsorbed for the first layer and that a subsequent layer is adsorbed, obeying the law of the adsorption isotherm. It seems probable that if the adhesive forces between the adsorbent and gas are strong, a factor determined both by the nature of the adsorbent as well as of the gas, that the unimolecular layer will still possess the power of adsorption although more feebly developed. For strong adsorbents dealing with gases which are highly polar in character and near their critical point, layers several molecules thick may readily be imagined to exist. If the gas be below the critical temperature, multimolecular layers can apparently be built up with ease, provided that the pressure be high enough. It may be noted that Hardy's investigations on the effect of substances such as octyl alcohol on the coefficient of frictions between metal surfaces likewise leads to the conclusion that octyl alcohol when vaporised over a metal surface is adsorbed to form a thick film in which the secondary layers are much less strongly adherent than the primary film

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[1] *Loc cit*

The question whether a gas can, when it is maintained above the critical temperature, build up a second or more layers on augmentation of the pressure, is as yet uncertain Indirect experimental evidence for the multimolecular nature of films of vapours adsorbed on solids is provided by the heats of adsorption But, as we shall have occasion to note subsequently, the surface of the catalyst is by no means uniform in nature, part possessing strong adsorbing powers with other portions of varying activity, a variation in the amounts of different gases adsorbed at what are apparently saturation pressures may indicate, not films of varying thickness, but a covering of varying fractions of the total exposed surface

We may conclude that at solid as well as at liquid surfaces primary adsorption is accompanied by a marked decrease in free energy The building up of secondary or multimolecular films is, however, a by no means uncommon phenomenon, especially in the case of vapours on strong or powerful adsorbing agents, whilst the forces operating in the formation of the primary unimolecular film are strong, those in the secondary film are weaker The primary forces may be compared to the valency forces operative in co-ordination compounds, whilst those in the secondary film are more akin to the cohesional forces operative in vapours and liquids As an indication of the magnitude of the primary forces may be cited the following data on the average heats of adsorption of gases on metals, these gases in all probability forming but primary films in contact with the metals under consideration

Gas	Metal	Q cals per grm mol
H_2	Pd	18,000[1]
	Pt	13,760[1]
	Ni	11,800[2,3]
	Cu	9,500[4]
C_2H_4	Ni	5,845[3]
C_2H_6	Ni	5,000[3]
CO	Pt	32,000[4]
	Cu	28,000

A closer investigation of the heats of adsorption of gases reveals an interesting phenomenon, namely, that the heat of adsorption is not a constant value for a particular gas and metal, but is dependent on the state of the surface of the metal; highly active metals adsorb gases more readily and possess a higher heat of adsorption. Since, in general, metals prepared at low temperatures possess composite surfaces, the heat of adsorption gradually falls as the more active portions become covered with the gas, resulting in a " spread " of the heat of adsorption. Values ranging from 33,000 to 11,000 calories per grm.-molecule have been obtained for the heat of adsorption of hydrogen on nickel. Similar data are available for carbon monoxide on copper. This " spread " of the heat of adsorption with the pressure is, as we shall note, of importance in attempts to elucidate the nature of the catalyst surface.

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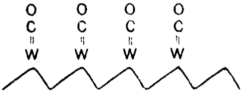
[1] Mond, Ramsay, and Shields, *Zeitsch physikal Chem*, 1898, **25**, 657

[2] Beebe and Taylor, *J Amer Chem Soc*, 1924, **46**, 43

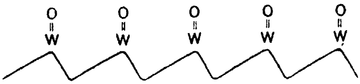
[3] Foresti, *Gazz Chem Ital*, 1923, **53**, 487

[4] Langmuir, *Trans. Farad Soc*, 1921, **17**, 641.

Orientation at solid surfaces.—If the indirect measurements of the surface energies of solids are in any way reliable, their surface energies are much greater than for liquids, and it is to be anticipated that adsorption at the surface of solids will result in the formation of a similar layer of orientated molecules. Evidence for this assumption is provided in a number of cases. Langmuir[1] has made an exhaustive study on the adsorption of gases on metallic filaments at low pressures, and has come to the conclusion that definite structural formulæ can be given to the adsorbed layer. Thus, carbon monoxide is strongly adsorbed by tungsten filaments at relatively low temperatures; the union between the carbon monoxide and the tungsten is so great that the whole group (WCO) distils off as a single molecule. At high temperatures, however, the union between metal and gas is by no means so strong, and carbon monoxide is removable unchanged. These experiments, together with the quantitative data on adsorption in a unimolecular layer, lead us to picture a type of adsorption film



Again, small traces of oxygen completely inhibit the action of a hot tungsten wire on the dissociation of hydrogen at high temperatures; the adsorbed oxygen is likewise not reduced by hydrogen, although tungstic oxide is readily reduced. The union of tungsten and oxygen in the adsorbed film must evidently be a very close one, and may perhaps be diagrammatically represented as



The union of these simple gases to metals thus appears similar in nature to a chemical union, which similarity we noted in discussing the data on interfacial surface tension; the data there presented indicated that mercury behaved in a similar manner in respect to a decrease in free energy when molecules containing reactive groups are brought in contact with it. There appears little doubt that ethyl iodide, for example, is anchored to the mercury by attachment to the iodine. The investigations of Hardy[1] on the effect of small traces of fatty acids and alcohols on the lubricating properties of a hydrocarbon oil for glass and metal surfaces, indicate also in a striking manner that these organic derivatives are attached by their "polar" $-COOH$ and $-CH_2OH$ groups to these solid surfaces. It may be noted in confirmation of these views that alcohol readily displaces hydrocarbons from the surface of metals such as copper.[2] Similar conclusions as to the orientation of fatty acids on sheets of mica have been arrived at by Sir William Bragg and his co-workers,[3] where it was found that acids allowed to solidify on mica sheets solidified in strata of regular orientated molecules, the direction of orientation being perpendicular to the plane of the mica. Perhaps one of the most convincing pieces of evidence in favour of the hypothesis of orientation on adsorption at the surface of solids is provided by the data of Palmer and Constable on the decomposition rate of a series of primary alcohols at a copper surface according to the reaction $RCH_2OH \rightarrow RCHO + H_2$. The following data are cited from their experiments.

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[1] *Loc. cit.*

Catalyst Copper	Velocity of Decomposition (t 20)	Temperature Coefficients for 10° at 250° C
I Ethyl alcohol	0.169	1.533
Butyl alcohol	0.169	1.543
II Ethyl alcohol	0.258	1.531
Propyl alcohol	0.246	1.546

In spite of the marked alteration in the length of the hydrocarbon chain attached to the $-CH_2OH$ group the velocity and temperature coefficient for the alcohols on a specific catalyst are identical, confirming the hypothesis that the $-CH_2OH$ group is the only part of the molecule taking part in the reaction with the copper.

In the above example orientated adsorption occurs in such a manner that the conditions for accelerated reaction are favourable. It is clear that cases may arise, especially in bimolecular surface actions, where the orientation of the adsorbed molecules is such that reaction cannot proceed between the reactive groups. Cases of this character have been investigated by Kruyt and Van Duin,[4] the alkaline saponification of esters and the addition of bromine to sodium p-sulpho cinnamate are retarded by charcoal, although both reactants are adsorbed on the surface. The removal of bromine from $\alpha\beta$ dibromo propionic acid by means of potassium iodide, on the other hand, is accelerated by the presence of charcoal.

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[1] *Proc. Roy. Soc.*, 1922, **100**, 550, **401**A, 487.

[2] Pockels, *Wied. Ann.*, 1899, **17**, 669.

[3] Muller and Shearer, *J. Chem. Soc.*, 1923, **123**, 3156.

[4] *Rec. trav. chim.*, 1921, **40**, 2, 249.

Again we shall note that, in discussing the effect of pressure on the velocity of such heterogeneous catalytic actions, we shall be led to considerations as to the "valency" of the adsorption compound formed in the primary layer. Anchoring of the adsorbed molecule may take place on several underlying atoms of the catalyst.

The "availability" of surfaces.—We have noted that Langmuir assumed that the adsorbing surface consisted of a uniform space lattice, each elementary space being the seat of a directive adsorptive force or a potential chemical covalent bond A more detailed examination, however, reveals the fact that the surface is by no means so uniform as imagined, and that the irregularities are of dominant importance in catalytic reactions. Langmuir himself considered, abstractly, adsorption at a surface non-uniform in character. It is the results of catalytic study which give concreteness to such a consideration

We must note that the coarse macro-crystalline surfaces are less active than surfaces prepared at low temperatures If we consider, in the first instance, the chief components of a metal catalytic surface, namely, the edges, corners, and faces of the innumerable small crystals present in the surface, we can draw certain conclusions as to the lack of uniformity, not only in the surface, but also in the surface energy, from crystallographic data Bravais was the first to note that the planes of a crystal which were most densely packed and were also separated from the neighbouring parallel plane most widely, were those which appeared most frequently, and also that a closely packed surface was usually associated with a wide interplanar distance, and *vice versa*. Later, Gibbs indicated that the most stable planes in a growing crystal were those possessing the least interfacial surface energy.

Although crystal growth rate is markedly affected by such factors as rates of diffusion, local temperature differences, minute alterations in density of the solution, yet, as the investigations of Valeton,[1] Niggli,[2] and Tertsch [3] have indicated, the evidence for a surface energy varying with the closeness of the surface packing is extremely strong. In a similar manner it can readily be shown from a study of the vapour tensions and solubilities of so-called amorphous substances that the atoms at the edges and corners, including those in the corners of the steps on a growing crystal as indicated in the diagram, possess greater adhesional force for gases and liquids than atoms situated in the planes of the crystal facets In addition to this micro-crystalline material present in a metal surface there are present a number of isolated atoms, and groups of atoms which are not in a space lattice and may be designated as amorphous material These are, as anticipated, even more reactive, as far as adsorption and solution are concerned, than the crystals themselves

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[1] *Phys. Rev.*, 1920, **21**, 106.

[2] *Zeitsch. anorg. Chem.*, 1920, **110**, 55.

[3] *Zeitsch. anorg. Chem.*, 1924, **136**, 205.

Attention may be directed to the alteration in several physico-chemical properties of materials subjected to extreme subdivision. Thus we have data which indicate that the heats of solution, heats of vaporisation, vapour pressures, dissociation pressures, solubilities of finely comminuted substances, exceed those of the substances in bulk

This phase is consequently metastable in comparison with the regular crystalline variety, and consequently will slowly revert back to the more closely packed form In the case of metals the rate of conversion at ordinary temperatures is relatively slow, but on elevation of the temperature these amorphous or irregularly situated atoms readily slip back into the more stable configuration of the space lattice of the element, a process termed sintering The sintering temperature—*i e* the temperature at which the rate of conversion becomes rapid—varies markedly with different metals, and should of course give an approximate value of the energy of the atomic adhesion of the metal Smith[1] gives the following values for the sintering temperatures of a number of metals.

Metal	Sintering Temperature ° C
Pt black	500
Pt ppt	700
Pd black	600
Ppt Cu	250
Ppt Ni	700
Ppt Ag	180
Au	200
Co	200
Reduced Co	500

Judged by loss of adsorptive capacity of the reduced metal sintering may take place at much lower temperatures than thos recorded by Smith This loss of adsorptive power is much the mos sensitive index of change of surface on heating[2]

The process of sintering is followed by the growth of the minute crystal to larger ones which become microscopically visible in annealed metals

Associated with these changes in surface from the unordered an micro-crystalline to the macro-crystalline we find a marked decreas in catalytic activity and in adsorptive power. The following dat show the effect of sintering on the adsorption of hydrogen and ethylen on copper and nickel determined by Pease[3] and by Beebe and Taylor:[4]

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[1] *J Chem Soc*, 1923, **123**, 2008

[2] Taylor, 3rd Report on Cont Cat., *J Phys Chem*, 1924, **28**, 912

[3] *J Amer Chem Soc*, 1923, **45**, 1193, 2296 [4] *Ibid.*, 1924, **46**, 43

Metal.	Temperature of Reduction ° C.	Adsorption of Gas in c.c. per grm. at N.T.P.	
		H_2.	C_2H_4.
Cu . . .	200	3·70	8·45
	450	1·15	6·85
Ni . . .	300	35·0	. .
	400	16·0	. .

That the surface of a catalyst is composite in character is likewise indicated from the fact that the saturation capacity is not identical for all gases. We have already referred to the fact that many vapours may be adsorbed in multimolecular layers but that in gases unimolecular films are to be expected. Under these conditions the saturation capacity of a catalyst should be identical for all gases; this is evidently not the case, for, as we note from the figures cited above, ethylene is more strongly adsorbed than hydrogen, and the saturation capacity for the former gas is not reduced so much on sintering.

That this view is probable may be deduced from data on the adsorption of hydrogen by nickel at various temperatures and pressures. From a study of the adsorption isotherms, Gauger and Taylor[1] showed that at relatively low partial pressures of hydrogen an apparent saturation of the surface was reached. Thus at 25° C. and 75 mm. pressure, a given sample of nickel adsorbed 8·7 c.c. of gas. A tenfold increase of pressure did not increase the adsorption by one per cent. At 305° C. apparent saturation was reached at 250 mm. pressure, a threefold increase of pressure not measurably increasing the adsorption. But, at this temperature, the adsorption only amounted to 5·3 c.c. of gas. This spread in the amounts of gas adsorbed at the two temperatures, coupled with the observations made as to the attainment of approximate saturation of the surface, independent of marked pressure increase, is strongly suggestive of the conclusion that the atoms in the surface have varying capacities to hold gas adsorbed, dependent on their position in the surface. It suggests also that a surface atom capable of holding a gas at one temperature may be unable to do so at higher temperature.

It is probable that, on active metals, the "availability" of the surface varies from gas to gas. On the closely packed facets the adsorption forces are, as we have seen, much weaker than on the more open surfaces, and gases which are not readily adsorbed, such as the non-polar, more perfect gases, will not be adsorbed strongly on the crystal facets. On the other hand, polar and easily liquefiable gases will be adsorbed over the entire surface.

This differentiation in the strength of union between adsorbate nd adsorbent is also exemplified in the adsorption of oxygen at charcoal and some metal surfaces It is found, for example, that if oxygen be adsorbed on to a charcoal surface three types of surface compounds can be identified A small fraction of the oxygen may be removed as such by evacuation, a larger portion may be removed as carbon dioxide by exhaustion at relatively low temperatures, whilst a third more stable portion into which the other forms are gradually converted is only removed at very high temperatures in the form of carbon monoxide and carbon dioxide Whilst three forms of carbon surface, the diamond, the paraffin or chain, and the ethenoid (to which the black colour is due), are undoubtedly present, the alteration in the type or the strength of union between the superficial and the underlying carbon atoms is reflected in the alteration in the carbon oxygen linkage Rideal[1] noted that oxygen could be adsorbed on a nickel surface in two forms, one readily reducible by hydrogen at low temperatures, and the other similar to a superficial coating of nickel oxide only reducible at relatively high temperatures These observations have been extended and confirmed by Larson[2] in the case of copper

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[1] *J. Amer. Chem. Soc.*, 1923, **45**, 920.

The evidence for a variability in the character of a catalyst surface is provided not only from considerations in respect to crystal structure and the adsorption of gases, but also from experimental data on the rate of catalytic change Such evidence is provided from two different considerations We may on the one hand, calculate the rate of condensation of reactants and rate of evaporation from the catalyst surface with the aid of the Herz-Knudsen equation and a knowledge of the amount of gas adsorbed under the experimental conditions, and compare this theoretical maximum rate of reaction with that actually observed It will be found that but a minute fraction of the molecules adsorbed on the surface actually undergo chemical reaction, this fraction is found to vary with the nature of the catalyst surface and is not dependent on the energy of activation of the reaction as is exemplified by the following data of Hinshelwood and Topley[3] on the decomposition of formic acid into carbon dioxide and hydrogen at various surfaces

Surface	Energy of Activation Cals per mol	k at 200° C
Duroglass	24,500	$2{\cdot}5\ 10^{-7}$
Gold	23,500	$9{\cdot}2\ 10^{-6}$
Silver	31,000	$1{\cdot}03\ 10^{-5}$
Platinum	22,000	$4{\cdot}4\ 10^{-4}$
Rhodium	25,000	$2{\cdot}4\ 10^{-3}$
Palladium	39,000	$1{\cdot}0\ 10^{-3}$

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[1] *J Chem Soc*, 1922, **121**, 318

[2] *J Amer Chem Soc*, 1925, **47** 354

[3] *J Chem Soc*, 1923, **123**, 1014

Evidently the catalytically active patches are greater in extent on the metals of the platinum series than on silver and gold or duroglass, whilst the energies of activation are all comparable, with the exception of palladium.

Again, we find that on the addition of minute amounts of poisons to catalysts a very serious reduction in the reaction velocity occurs without any sensible diminution in the adsorption of the reactants taking place. Many cases of qualitative fractional and selective poisoning will be discussed in a subsequent section. A few quantitative experiments have been made on the relative areas of patches of varying activity; thus Rideal[1] found that 0·01 per cent only of a nickel surface was effective in catalysing the union of hydrogen and ethylene. Pease[2] noted that but a few cubic millimetres of carbon monoxide poisoned a copper surface for the same reaction. Rideal and Wright[3] found that on an active sugar charcoal 0·01 per cent of the surface was autoxidisable and 40 per cent of the surface was catalytically active.

Recent experiments by Richardson[4] on thermionic emission from metal surfaces have revealed the interesting fact that electron emission from a hot surface does not occur uniformly over the surface but apparently from localised patches It is an interesting speculation to associate these patches which are thermionically active with the active patches identifiable by adsorption and catalytic means.

That some connection may exist is evident from the experiments of Thompson,[5] who showed that thermionic emission commenced from a platinum wire when raised to the temperature at which the union of hydrogen and oxygen on the surface commenced. Langmuir[6] likewise noted that when sufficient poison had been admitted to a reacting system containing a catalytic tungsten wire to suppress the catalysis, thermionic emission was simultaneously suppressed.

Activation of metal surfaces.—In the foregoing sections we have discussed somewhat briefly the evidence in favour of the hypothesis that catalysis occurs on localised reaction centres which may be relatively small in area compared to the total surface exposed to the reactants. These localised reaction centres are characterised by strong adsorbing powers, as is exemplified by the behaviour of traces of poisons on the reaction velocity; whilst these in turn are related to the configuration of the metal surface, an open packing or irregular atomic distribution being more effective than a closely packed surface. These conclusions throw light on the process of activation of a metal surface. It is well known that repeated alternate oxidations and reduction at low temperatures render metals such as copper, iron, and nickel extremely active. An investigation on the increase in catalytic activity of copper for the dehydrogenation of ethyl alcohol after a series of oxidations and reductions at 250° C. showed that if precipitated copper oxide were utilised as source of copper a marked increase in catalytic activity was to be observed after two reduction processes had been completed, subsequent oxidations and reductions scarcely affecting the catalytic activity. In the first reduction copper is formed from cupric oxide, and a skeleton of metal pseudomorphic with the original copper oxide results. Dunn[1] has shown that this "open" variety of copper is stable up to 400° C., at higher temperatures it commences to sinter and reverts back to the more closely packed configuration of metallic copper, with a corresponding reduction in permeability to gases and catalytic activity. On the second oxidation, cuprous oxide is formed which, on reduction, yields an even more open network of copper. Subsequent oxidations and reductions do not open the lattice any further, and it has been noted that even a small decrease in catalytic activity may occur, due to collapse of the open structure. This artificial increase in the relative area of active surface must be distinguished from an increase in the total surface area by artificial means, an increase which may be associated with a relative decrease in the fraction of surface catalytically active, a point which we shall have occasion to discuss in a subsequent section.

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[1] *Loc cit.*

[2] *J. Amer. Chem Soc*, 1923, **45**, 1193, 2296.

[3] *J Chem Soc*, 1925, **127**, 1347.

[4] *Proc. Roy. Soc.*, 1925, **107**A, 377

[5] *Physikal. Zeitsch.*, 1913, **14**, 11.

[6] *Loc. cit.*

The reaction velocity of catalytic changes.—In the preceding sections arguments have been advanced in support of the hypothesis that molecules adsorbed in the primary film are orientated and held relatively firmly. Such adsorption is orientated, since particular groups in complex molecules affect the values of the adhesional forces. In addition we have noted that only a small fraction of the surface even of an active material is catalytically effective.

Bodenstein[2] and Bodenstein and Stock[3] assumed that reaction proceeded in the adsorbed gas layer around the catalytic material which served merely to condense the gas in an atmosphere around the surface. The reaction velocity, on this view, was governed by the rate of diffusion of reactants or products through this adsorbed thick film the thickness of which was a function of the pressure. This point of view was shown to be untenable by Langmuir[4] for heterogeneous gaseous reactions, but, as we shall note, limitations due to rates of diffusion frequently play an important part in heterogeneous reactions in liquids.

It is found, for example, that the decomposition rate of certain hydrides is materially affected by the pressure of the gas, as is evident from the following data.

According to Bodenstein's view the film thickness should be proportional to the pressure for phosphine and arsine, and proportional to the square root of the pressure for hydrogen and ammonia.

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[1] Unpublished experiments.

[2] *Zeitsch physikal Chem*, 1899, **29**, 665.

[3] *Ber*, 1907, **40**, 570.

[4] *J. Amer Chem Soc*, 1916, **38**, 2280.

Gas.	Surface.	Reaction Rate.	Investigator.
H_2	Tungsten	$\frac{dx}{dt} = K\sqrt{P}$	Langmuir, *loc. cit.*
PH_3	Phosphorus	$\frac{dx}{dt} = KP$	Koos, *Zeitsch. physikal. Chem.*, 1893, **12**, 155. Trautz, *Zeitsch. anorg. Chem.*, 1919, **106**, 95
AsH_3	Arsenic	$\frac{dx}{dt} = KP$	Cohen, *Zeitsch. physikal. Chem.*, 1896, **20**, 303 ; 1898, **25**, 483
SbH_3	Antimony	$\frac{dx}{dt} = KP^{0.6}$	Stock, *Ber.*, 1918, **41**, 1319
NH_3	Quartz glass	$\frac{dx}{dt} = K\sqrt{P}$	Bodenstein, *Ber.*, 1907, **40**, 570

Langmuir showed, from a consideration of the observed reaction velocity and the rate of condensation of the gas on the catalyst surface, that " the velocity is in general not fast enough materially to affect the equilibrium between the adsorbed film and the surrounding gas ". We must imagine that in such reactions molecules are continually hitting the surface, condensing there, and after a time interval more or less short either evaporating unchanged or undergoing decomposition with subsequent evaporation of the reaction products. Before attempting to analyse in more detail the mechanism by which a condensed molecule selectively re-evaporates unchanged or undergoes surface decomposition, we find that Langmuir's point of view affords valuable evidence as to the structure of the adsorption compound that is formed on condensation of the reactant. This evidence, together with the inference as to the points of attachment derived from the considerations previously advanced, gives us a relatively good picture of the structure of the surface compound. In the case of the surface catalytic decompositions referred to above, there are evidently two extremes : either the surface, *by which is meant the catalytically active surface*, is covered only to a small extent with the reacting gas, or it may be almost completely covered.

In the first case we may, on analogy with our previous considerations (p. 35), write

$$\text{Rate of condensation of unchanged gas} = \alpha\mu \, ;$$

$$\text{Rate of evaporation of unchanged gas} = \nu_1\theta^n,$$

where n represents the number of elementary spaces on the surface occupied by each molecule of the reactant and θ is the fraction of surface covered.

The product of chemical reaction is formed by the combination of molecules from m adjacent spaces.

If $\frac{dx}{dt}$ represents the velocity of chemical change,

$$\frac{dx}{dt} = \nu_2\theta^m.$$

Hence
$$\frac{dx}{dt} = \nu_2\left(\frac{au}{\nu_1}\right)^{\frac{m}{n}}.$$

The velocity thus varies as the m/n power of the gas pressure. In the case of the dissociation of hydrogen on tungsten Langmuir found $\frac{m}{n} = \frac{1}{2}$, whilst for the recombination of hydrogen atoms on tungsten he found $\frac{m}{n} = 2$. These relationships are at once intelligible if it be assumed that a hydrogen atom occupies or is attached to but one elementary space on the lattice, the hydrogen molecule would thus occupy two spaces. Whilst absolute values cannot be assigned to m or n in such cases as in the decomposition of the hydrides, it is clear that in cases such as the decomposition of phosphine where $m = n$, diagrammatic representation is possible by assigning a value of $m = n = 2$ for the reaction.

On this view of valency of adsorption compounds, stibnine, which at low temperatures possesses an exponent of 0.6, must be assumed to undergo a composite reaction, for it is clear that m/n must be some simple fraction or integer. This is confirmed by the fact that the exponent rises to unity with elevation of the temperature. It is possible that stibnine undergoes two types of surface reaction, one similar to that of ammonia on quartz glass, and the other comparable to that of arsine, the latter predominating at high temperatures.

We have noted that there exists another case of simple decomposition at a catalytic surface in which the surface is completely covered. Under these conditions the surface concentration will be constant and independent of the pressure; thus, the reaction velocity will be independent of the pressure and depend only on the extent of catalytically active surface. A number of reactions of such a type corresponding to a reaction of zero order have been examined, such as the decomposition of alcohols at a copper surface and the decomposition of formic acid at solid surfaces.

Multimolecular surface actions. Similar considerations may be applied to the more complicated interactions, catalytically accelerated at solid surfaces. A number of these have been examined in detail, such as the oxidation of sulphur dioxide to trioxide at the surface of platinum,[1] the oxidation of carbon monoxide at the surface of quartz[2] and of platinum,[3] and the hydrogenation of ethylene at nickel surfaces,[4] and also at copper surfaces.[5]

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[1] Bodenstein and Fink, *Zeitsch. physikal. Chem.*, 1917, **60**, 1.

[2] Bodenstein and Ohlmer, *ibid.*, 1905, **53**, 175.

[3] Langmuir, *J. Amer. Chem. Soc.*, 1915, **37**, 1162; *Trans. Farad. Soc.*, 1921, **17**, 621.

[4] Palmer, *Proc. Roy. Soc.*, 1921, **99**A, 402; Rideal, *J. Chem. Soc.*, 1922, **39**, 309.

[5] Pease, *J. Amer. Chem. Soc.*, 1923, **45**, 1193, 226.

r or the oxidation of carbon monoxide Bodenstein and Ohlmer fou
e following reaction velocities:

$$(a)\ \text{On crystalline quartz}\quad \frac{dx}{dt} = KP_{CO}\sqrt{P_{O_2}}.$$

$$(b)\ \text{On quartz glass}\quad \frac{dx}{dt} = \frac{K'P_{O_2}}{P_{CO}}.$$

we assume that on crystalline quartz the carbon monoxide occupi
e elementary space on the lattice we obtain for the conditions
quilibrium

$$\alpha_1\mu_1 = K_1\theta_1.$$

r the oxygen which we assume occupies two elementary spaces,

$$\alpha_2\mu_2 = K_2\theta_2^2.$$

action takes place between adjoining carbon monoxide molecul
d oxygen atoms, or

$$\frac{dx}{dt} = k_3\theta_1\theta_2$$

$$= KP_{CO}\sqrt{P_{O}}$$

quartz glass, on the other hand, the adsorptive forces are apparentl
onger at the localised active patches, and we must assume that thes
tches are almost completely covered with an adsorbed film of carbo
monoxide. The rate of condensation of this gas will be

$$\alpha_1\mu_1\theta,$$

l since θ is small and constant we obtain

$$\alpha_1\mu_1\theta = k_1$$

e oxygen undergoes reaction when its molecules come into contact
h the uncovered surface; thus the rate of reaction will be

$$\frac{dx}{dt} = k_2\theta\mu_2$$

$$= k_2\mu_2\left(\frac{k_1}{\alpha_1\mu_1}\right) = K\frac{P_{O_2}}{P_{CO}}.$$

In addition to these simple cases many more complicated examples
e been worked out on the general principles laid down by Langmuir.
ention may be drawn to three phenomena occurring in such surface
ctions, which appear to be by no means uncommon.

(*a*) *Reaction by contact with an adsorbed molecule or atom.*—
gmuir[1] has shown that carbon monoxide undergoes oxidation at
latinum surface chiefly by striking atoms already present on the
face as a result of adsorption of oxygen molecules on two elementary

spaces There is some new evidence obtained by Wolfenden[1] which indicates that some hydrogenation processes occur by collision of reactants with hydrogen atoms present on a metal surface, though it seems also that not all hydrogenation processes may be so achieved[2]

(*b*) *Inhibition by reactants* —We have noted that the *general* equation for a reaction between two gases on a surface which does not adsorb either reactant very strongly can be expressed in the form

$$\frac{dx}{dt} = K\theta_1^n\theta_2^m,$$

where θ_1, θ_2 represent the fractions of the active surface covered by the respective *n* and *m* valent reactants

If the surface be almost completely covered with both reactants

$$\theta_1 + \theta_2 = 1,$$

whence $$\frac{dx}{dt} = K\theta_1^n(1 - \theta_1)^m.$$

Thus, the reaction velocity will be at an optimum for a particular ratio of the reacting gas pressures sinking on either side of this optimum as the ratio of the reactants is increased or decreased The existence of this optimum has been shown for ethylene and hydrogen at a copper surface by Pease, at a nickel surface by Rideal, and at a charcoal surface in the oxidation of oxalic acid by Rideal and Wright

(*c*) *Inhibition by the reaction products* —In the case of the hydrogenation of ethylene the ethane produced does not exert any inhibiting action, but many cases are to be found in which the reaction products are strongly adsorbed and thus slow down the reaction velocity. Thus, Bodenstein and Fink noted the inhibiting action of sulphur trioxide on the oxidation process of the dioxide at the surface of platinum, Burk and Hinshelwood[3] that of hydrogen in the decomposition of ammonia, and Hinshelwood and Pritchard[4] of oxygen on the decomposition of nitrous oxide at platinum surfaces

We may divide these cases into two classes, those in which the reaction product is very strongly adsorbed, and those in which it is adsorbed relatively as strongly as the reactants As an example of the former we may take the case of the oxidation of sulphur dioxide. We may imagine the catalyst surface covered with a layer of SO_3 molecules each occupying two elementary spaces

The rate of condensation will be $\alpha\mu\theta^2$ and the rate of evaporation ν will be constant, since the surface is nearly completely covered

Since equilibrium obtains

$$\nu = \alpha\mu\theta^2$$

In the presence of excess oxygen any vacant spaces on the active catalyst will be occupied by this gas, and the sulphur dioxide enters into reaction when it strikes the space occupied by the oxygen at a rate proportional to $\theta\mu_{SO_2}$. Hence we obtain

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[1] *Proc Roy Soc*, 1926, **110A**, 465

[2] Taylor and Marshall, *J Phys Chem*, 1925, **29**, 1140.

[3] *J. Chem Soc*, 1925, **127**, 1105

[4] *J. Chem. Soc*, 1925, **127**, 331.

$$\frac{dx}{dt} = \nu_2(\theta\mu_{SO_2}) = \nu_2\mu_{SO_2}\sqrt{\frac{\nu}{\alpha\mu}} = K\frac{P_{SO_2}}{\sqrt{P_{SO_3}}}.$$

In the presence of excess sulphur dioxide the reaction velocity will evidently be $\frac{dx}{dt} = K\frac{P_{O_2}}{\sqrt{P_{SO_3}}}$, in agreement with the experimental data of Bodenstein and Fink.

In the decomposition of nitrous oxide at a platinum surface, according to the equation

$$2N_2O \rightarrow 2N_2 + O_2,$$

Hinshelwood and Pritchard[1] found that oxygen exerted a retarding influence. If θ be the fraction of the active surface covered with the oxygen film at equilibrium, the rate of condensation and evaporation will be equal, or

$$\alpha\mu(1-\theta) = \nu\theta,$$

whence

$$1-\theta = \frac{\nu}{\nu+\alpha\mu} = \frac{1}{1+b(O_2)}.$$

The rate of decomposition of nitrous oxide on the bare catalytic surface will be accordingly

$$-\frac{dN_2O}{dt} = k(N_2O)(1-\theta) \text{ or } \frac{kN_2O}{1+b(O_2)},$$

or

$$\frac{dx}{dt} = \frac{K(a-x)}{1+bx},$$

where a is the original pressure of the nitrous oxide. The agreement between the observed values and those calculated with the aid of the above equation is shown in the following table:

P_{O_2}.	$\frac{dx}{dt}$ calc.	$\frac{dx}{dt}$ observed
23	46	44
40	35	36
745	29	26
112	20	20
159	14	15
206	10	12·5
257	10	10·4
305	10	9

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[1] *J. Chem. Soc.*, 1925, **127**, 331.

The reaction velocity in solutions.—In the case of heterogeneous catalytic gas reactions we have noted that the diffusion hypothesis of Faraday and Bodenstein could in general not be substantiated In all cases yet examined the observed surface reaction velocities are much smaller than the rate of contact of the gaseous reactants In solutions, however, and possibly also in cases where the surface reaction velocities are high, such as in the cases of surface combustion examined by Bone, the rates of diffusion may be comparable to the rate of chemical action It is clear that if the rate of diffusion be the limiting factor in such action, the influence of temperature on the reaction velocity will be that corresponding to the temperature coefficient of diffusion, which is small in gaseous and liquid media

Zero order reactions. It has already been observed that in many heterogeneous gas reactions, such as the decomposition of alcohols and esters at the surfaces of metals and metallic oxides, the rate of decomposition is independent of the pressure, an experimental fact readily intelligible on the assumption that the reactants are strongly adsorbed and that the reaction velocity actually measured is the rate of conversion of the adsorbed reactants and subsequent evaporation of the products. At sufficiently low pressures a departure from zero order reaction is to be anticipated Such zero order reactions are frequent in liquid systems We find, for example, that many enzyme reactions such as the hydrolysis of sugars as observed by Armstrong,[1] Hudson [2] and Nelson,[3] obey within wide limits such a law (see also Chap. XIII)

The case of the hydrogenation of unsaturated organic substances at colloidal and massive nickel and platinum surfaces presents some interesting features The reaction velocity of hydrogenation has been studied with a view to elucidation of the mechanism by a number of investigators, notably Paal,[4] Fokin,[5] Ubbelohde and Svanoe,[6] Thomas,[7] Rideal,[8] Armstrong and Hilditch [9] One of the factors unconnected with the mechanism of the reaction is the rate of supply of hydrogen by diffusion through the liquid to the catalyst surface It is found that this rate of supply is augmented by agitation, the rate of hydrogenation is determined over a limited range by the agitation rate n, and the relationship

$$\frac{dx}{dt} = Kn^2$$

is obeyed

A similar dependence of reaction velocity on the agitation rate was noted by Bredig and Teletow [10] in the decomposition of hydrogen peroxide at a platinum surface. In this case a limitation to the rate of reaction is set by the rate of diffusion of hydrogen peroxide through the "diffusion layer"[1] of water adhering to the platinum, the thickness of this layer being reduced under increased agitation. Above certain critical speeds, however, it is found that the rate of hydrogenation as well as the rate of decomposition of hydrogen peroxide is unaffected by the rotation speed, and the rate is thus not influenced by the rate of supply of hydrogen to the catalyst. An examination of the hydrogen uptake time curves indicates that with pure materials and active catalyst the curves are linear in character until the reaction is nearly completed, when a unimolecular form appears. With old and feebly active catalysts the zero order portion of the curve becomes smaller and the curve over an extended period of time acquires a unimolecular character. It has also been shown in the case of sodium cinnamate and sodium phenyl propriolate that these reactants are strongly adsorbed by a colloidal palladium catalyst. It appears that the rate of reaction in the hydrogenation of pure substances is proportional to the concentration of a ternary complex hydrogen-unsaturated compound-catalyst, similar to the many bimolecular surface gas reactions already discussed.

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[1] *Proc. Roy Soc*, 1924, **73**, 500

[2] *J Amer Chem. Soc*, 1908 **30**, 1160, 1564

[3] *Ibid*, 1916, **38**, 1109.

[4] *Ber*, 1907, **40**, 2309 . 1908, **41** 805

[5] *Zeitsch angew Chem* 1908, **22**, 1451 1492

[6] *Ibid*, 1919, **32**, 257, 276

[7] *J Chem Soc Inst*, 1920, **39**, 120

[8] *Trans Farad Soc* 1923, **19**, 1

[9] *Proc Roy Soc*, 1919 **96**A, 137 1920, **98**A, 27, 1921, **100**A, 240

[10] *Zeitsch Elektrochem.*, 1906, **12**, 581.

For organic substances strongly adsorbed at the catalyst surface the surface concentration will be independent of the bulk concentration; for substances feebly adsorbed and on inactive catalysts the surface concentration will be related to the bulk concentration by an equation of the Freundlich or Langmuir type. The reaction velocity will thus be independent of the bulk concentration until this falls to such a value that the surface concentration suffers a diminution. Poisoning by reaction products, gradual adsorption of poison from the reaction mixture, accumulation of impurities in the hydrogen, and other similar disturbances, readily cause a departure from the linear type of curve.

Uni- and pseudo-unimolecular reactions. Whilst over a large portion of the curve the reaction velocity of hydrogenation is of zero order with respect to the substance undergoing hydrogenation, the effects of variation of hydrogen pressure are by no means so definite. If the adsorption complex nickel-organic substance is relatively stable it is clear that, as in the ethylene hydrogen combination (Rideal and Pease), the reaction velocity should be proportional to the hydrogen pressure, a conclusion verified experimentally in simple cases by Armstrong and Hilditch. For low concentrations of catalyst the increase in rate is less than proportional to the increase in pressure, whilst it was found that if the unsaturated compound contained a group which had an affinity for nickel but was not open to hydrogenation, an increase in hydrogen pressure caused a more than corresponding increase in reaction velocity. The decomposition of hydrogen peroxide at the surface of massive platinum is, as we have noted, limited over a certain range of speed of agitation by the rate of diffusion of the hydrogen peroxide through the diffusion layer, and is thus pseudo-unimolecular in character

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[1] See Noyes and Whitney, *Zeitsch. physikal. Chem.*, 1897, **23**, 689; Brunner, *ibid.*, 1900, **35**, 283; Nernst, *ibid.*, 1904, **47**, 52.

At the surface of colloidal metals and oxides such as platinum, manganese dioxide, cobaltic oxide, and copper oxide, Bredig and his co-workers[1] obtained an approximately unimolecular rate of decomposition in slightly alkaline solution There is, however, a relative increase in the velocity constant as the reaction proceeds, and, in addition, the temperature coefficient is relatively high (*ca* 2·4 for 10° C rise). These two facts cast doubt upon the hypothesis that the pseudo-unimolecular character of the reaction velocity is a measure of the diffusion rate of hydrogen peroxide through the diffusion layer It is more than probable that but a small portion of the colloidal particles are catalytically active, and that we are measuring the true rate of chemical reaction at the surface The phenomena associated with colloidal catalysts receive a more detailed consideration in a subsequent chapter (Chap. XIII)

There are many other examples of catalytic acceleration by massive and colloidal platinum to be noted in aqueous solutions. Thus, a number of ionic oxidations are accelerated by the metal, *e g.*

$Ti^{\cdots} + \dot{H} \rightarrow Ti^{IV} + H$	Diethelm and Forster, *Zeitsch. physikal Chem*, 1908, **62**, 129
$Co_2(CN)_6{}^{IV} + \dot{H} \longrightarrow Co(CN)_6{}''' + H$	Denham, *ibid*, 1910, **72**, 641
	Manchot and Herzog, *Ber Chem Ges*, 1900, **33**, 1742
$Cr^{\cdot\cdot} + \dot{H} \longrightarrow Cr^{\cdots} + H$	Jablczynski, *Zeitsch physikal. Chem*, 1908, **64**, 748

Whether these reactions are limited in respect to their velocity by diffusion or the specific surface chemical reaction rate, requires further investigation It is more than probable that the transition from one limitation to the other on agitation of the liquid, as noted in the case of hydrogen peroxide, may be obtained in these cases also

The energy of excitation.—In the case of bimolecular gaseous reactions we have noted the necessity for adopting the hypothesis of active or excited molecules, the energy of activation or excitation being provided by inelastic collision For heterogeneous reactions likewise a similar hypothesis is necessary, for a simple calculation indicates that but a small fraction of the molecules of a gas impinging on an active catalytic surface actually suffers decomposition We have noted that many such actions proceed with uniform velocity although the pressure of the gas or concentration of the reactant in solution may undergo wide variations, and it is inferred that the catalytic surface is strongly adsorbent. Thus, the increase in velocity of the reaction on elevation of the temperature will, as we shall note, for these reactions, be almost a true measure of the critical energy increment. In many reactions, the active surface may undergo alteration in area on elevation of the temperature; thus, poisons may be partially desorbed with consequent increase in active area; the temperature coefficient will in these cases be abnormally large. Again, the configuration of the surface of a sensitive catalyst may alter as the temperature is raised, due to the increased rate of sintering. In the case of heterogeneous bimolecular reactions, inferences from the temperature coefficient of the reaction are liable to be misleading; thus, if one reactant be strongly adsorbed and the other undergoes reaction when it strikes a vacant space on the catalyst surface, the temperature coefficient will yield merely a measure of the latent heat of adsorption of the strongly adsorbed reactant.

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[1] *Zeitsch. physikal. Chem*, 1899, **31**, 258, 1901, **37**, 1, *Ber.*, 1904, **37**, 798.

For simple surface reactions, however, proceeding under conditions so that the surface is always saturated, the calculation of the energy of excitation yields approximately correct values. In the cases fulfilling these conditions, which have been examined with care, it is found that the energy of excitation of the catalysed reaction is always less than that of the uncatalysed homogeneous bimolecular gas reaction.

Thus, in the decomposition of nitrous oxide, which occurs both as a bimolecular homogeneous gas reaction and on the surface of platinum, Hinshelwood and Pritchard[1] found for the homogeneous reaction both from the temperature coefficient and from the relationship

$$\frac{\text{Number of effective collisions}}{\text{Total number of collisions}} = e^{-\frac{E}{RT}},$$

a value of $E = 55{,}000$ cals., whilst from the temperature coefficient of the surface reaction a critical energy increment of 32,500 calories per grm.-mol. was found. Rideal and Norrish[2] found for the homogeneous gas reaction $H_2 + \frac{1}{2}S_2 = H_2S$, a critical increment of 51,460 cals.; for the surface action between hydrogen and sulphur, a value of 25,750 cals.

Hinshelwood has pointed out that in the case of simple decomposition of N_2O, HI, and Cl_2O, for the surface reaction the activation of one molecule takes place, but, in the bimolecular gas reaction, the critical energy increment to be supplied must be sufficient to activate two molecules of the reacting species. The acceleration produced by such a conversion from a bimolecular to a "unimolecular" reaction is thus clearly intelligible, although the actual energy of excitation per gram-molecule may be very similar in the two cases.

In the case of homogeneous bimolecular reactions the energy of excitation is supplied by collision between the molecules. It might be suggested that only those molecules hitting the active catalyst surface with kinetic energy equal to or in excess of the critical value undergo activation and decomposition, the remainder merely condensing and undergoing subsequent evaporation

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[1] *J. Chem. Soc.*, 1925, **127**, 330.

[2] *J. Chem. Soc.*, 1923, **123**, 3216.

There are, however, several alternative possibilities which cannot lightly be dismissed Thus, we may consider that an adsorption compound is first formed between catalyst and reactant, and that this compound is subsequently supplied with activating energy by collision or by radiation Again, the actual act of adsorption may result in the production of an activated species The kinetic energy of the accompanying molecule, the surface energy of the catalyst, and the change in internal energy of the surface and adsorbate consequent on the formation of the surface complex may all contribute to such activation The specificity and localised activity of catalysts, as well as the extreme rapidity with which the kinetic energy of a colliding molecule is damped on collision with a solid surface (Langmuir), favour the view that the activation occurs in the catalyst-gas complex.

The relationship between evaporation and decomposition of an adsorbed molecule may be suggestively considered in the following manner The number of molecules evaporating per second per unit area of active surface at a temperature T may be written, if such surface be covered at all temperatures,

$$N\nu e^{-\frac{Q}{RT}},$$

where N is the number adsorbed and $\frac{1}{\nu}$ the mean life of an adsorbed molecule after activation with a quantity of energy Q, the latent heat of evaporation The number of molecules per unit area of active surface undergoing decomposition per second will be

$$N\nu' e^{-\frac{E}{RT}},$$

where $\frac{1}{\nu'}$ is the mean life of a molecule after activation with E, the critical energy increment for decomposition

The mean lives $\frac{1}{\nu}$ and $\frac{1}{\nu'}$ of the complexes between excitation and evaporation or disintegration correspond to Maxwell's period of molecular relaxation, since not only are vacant spaces filled up immediately, but the adsorbed molecules may be regarded as akin to a two-dimensional gas possessing purely vibrational energy in one vertical plane. The time of molecular relaxation in a homogeneous gas is $\frac{1}{\eta\Delta}$, where η is the viscosity and Δ the density, and thus varies but slowly with the temperature Since the process of readjustment of the distribution of energy in the surface phase after evaporation or disintegration is the same, it is probable that the mean lives are extremely short and possibly related to Q and E by the relationship $Q = Nh\nu'$, $E = Nh\nu'$, as suggested on p. 41.

Even more complex are cases such as the decomposition of alcohols, esters, and formic acid, the surface compounds of which may undergo evaporation, and two different types of surface decomposition each with its own characteristic critical energy increment for the particular catalyst employed. The fact that the rates of the two modes of decomposition are in no way related to the critical energy increments is clearly in favour of the hypothesis that we are dealing with two surface compounds of different character and structure, each of which may undergo the evaporation change but only one form of decomposition. It is to be anticipated that the heats of adsorption to form these two species of compounds would be different, and the hypothesis of the existence of these two types might thus receive experimental confirmation.

Apparatus employed.—The most important heterogeneous catalytic reactions include those in which the reactants are forced through a bed of granular contact material, the effluent gases or liquids being then submitted to analysis. Many examples of such reactions are to be found in technical practice, such as the catalytic process for the preparation of ammonia, hydrogen from water gas, the removal of calcium and magnesium salts from hard waters by sodium zeolites or chlorine from hydrochloric acid. The advance to be recorded in the scientific investigation of the hydrodynamics of the problem is not considerable.

It is at once evident that if a volume V of reactants be passed through a volume v of material per hour, the "space velocity" or the volume of gas passed through unit volume of catalyst is $\frac{V}{v}$ litres (or c.c.) per litre (or c.c.) per hour. The "space velocity" (or S.V.) is an important characteristic, especially for technical purposes, and a clear statement of the space velocity is necessary when the feasibility of any process is under discussion. A closer analysis of this definition will, however, indicate that there is some uncertainty about the details of this conception. It must be understood that the S.V. (space velocity) is always referred to the reactants at normal temperature and pressure, a matter of considerable importance when the reaction takes place in the vapour or gaseous state at elevated temperatures. Again, the conception of "reactant" permits of a certain degree of latitude. Thus, in the synthesis of ammonia from nitrogen and hydrogen in the stoichiometric ratios 1 : 3 both the gaseous constituents take part in the reaction, and since the stoichiometric relations are not altered after catalysis, both gases are to be considered as reactants. In other cases, such as in processes of hydrogenation, of selective combustion, or of the conversion of water gas into hydrogen and carbon dioxide in the presence of steam, the question arises as to whether the S.V should be referred entirely to the reactant, *i.e.* the substance undergoing hydrogenation or combustion, or again to the carbon monoxide in the water gas Thus, in the case of the water-gas conversion, the quantity of hydrogen in the gas or of steam employed might conceivably modify profoundly the velocity of reaction at the surface of the catalyst.

The procedure generally adopted is to refer the S V. to some important constituent of the reactants. Thus, in the water-gas reaction, the S V. may be taken from the mean of the total volume of gas entering and leaving the catalyst mass corrected to N.T.P after condensation of the steam, whilst in cases of hydrogenation of, say, an oil, the S V. would be referred to the mass of oil hydrogenated per unit volume of catalyst space or per unit mass of catalyst.

From the space velocity a second figure, no less important for technical operations, may be obtained, namely, the "space time yield" (or S T Y) If the fractional conversion of reactants accomplished by a single passage through the catalyst mass at a space velocity of *V* be *R*, then the space time yield or the yield in litres of desired product per litre of catalyst space per hour will be *R V*. In many cases, for convenience, the S.T.Y is expressed in kilograms per litre of catalyst space per hour, or other similar units which give a numerical value to the product *R V*

It may be observed that there is a relationship between *R* and *V*, since for low values of *V* the equilibrium under the conditions of operation is arrived at and *R* attains its maximum value With an increase in the space velocity, equilibrium amongst the reactants may not have time to establish itself during the passage through the contact mass, and with exceedingly high space velocities the composition of the reactants will scarcely be affected by such passage Thus, to attain a maximum value of the product *R V*, it is not necessarily or indeed always desirable to limit the space velocity to such low figures as may be necessary to ensure attainment of equilibrium. Higher values for the S V. and a lower conversion may give a greater output per hour The *R V*, *V* curve will consequently assume some such form as the diagram (Fig 4).

(i.) The region *O* to *a*, in which equilibrium is established at all velocities up to a space velocity of *a′*, whence the product *R V* is proportional to *V*. (ii) The region *a* to *b*, where from space velocities *a′* to *b′* equilibrium is not established and the percentage conversion gradually falls off, the product *R V* increasing, however, with increasing values of *V*. (iii.) The region *b* to *c*, where, with exceedingly high space velocities, the rate of diminution of *R*, the fractional conversion, exceeds the rate of increase in the space velocity, with a consequent decrease in hourly output

In all circulating processes the optimum space velocity is represented by the point *b'* on the characteristic *R V*, *V* curve, whilst for non-circulating processes the maximum hourly output and the best utilisation of the reactants (in those cases where equilibrium conditions are desired) is attained at space velocities indicated by the point *a'*.

No satisfactory data have been published on the design of converters for such types of heterogeneous catalysis, but the following points which bear upon this subject may be mentioned.

We have derived a figure for the space velocity from a consideration of the rate of flow of the reactants through a given volume of catalyst space. This figure evidently gives us no information as to the actual velocity through that space, since part is occupied by the catalytic material. For purposes of calculation we may assume that the catalyst consists of a number of uniform spheres, and, further, that they are packed in a simple and regular manner in the catalyst chamber.

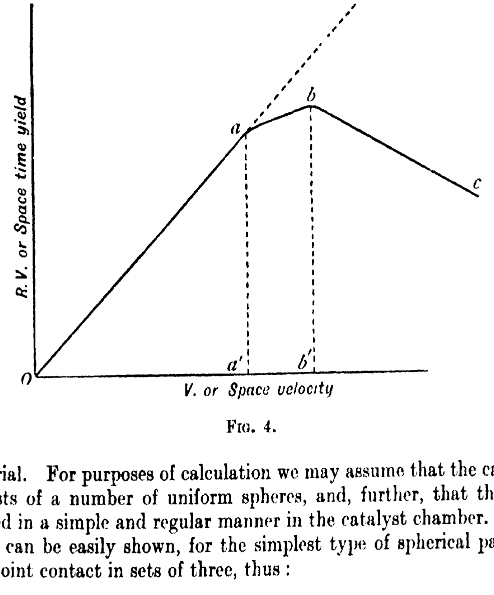
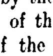


FIG. 4.

It can be easily shown, for the simplest type of spherical packing, viz. point contact in sets of three, thus:



that the free space unoccupied by the spheres (assumed inelastic and incompressible) is 33·5 per cent of the total volume occupied and is independent of the diameter of the spheres, whilst the free cross-sectional area is 9·55 per cent of the area of the catalyst chamber and is likewise independent of the diameter of the spheres. The dependence of the area of contact exposed by the surface of the spheres on the diameter of the individual is exemplified in the following curve (Fig. 5). The advantages of fine packing are clearly demonstrated

The works of O Reynolds on gravitational theory, and of Pope and Barlow on chemical crystallography, may be consulted for other types of spherical packing They will be of use in giving an orientation into the problems of arrangement of the catalyst bed, but their utility is limited by the deviations of the catalytic material from spherical shape

It is evident that for a S V of V the true space velocity is approximately $3V$, when due allowance is made for the space occupied by the catalytic material, and that the linear velocity in metres per second may be obtained by calculating the rate of flow in a tube one-tenth the cross-sectional area of the converter In technical design a linear flow rate of 10 metres per second is frequently taken as a convenient basis for calculation of gaseous reactions Although fine division of the catalyst is desirable from the point of view of increasing the superficial area per unit volume of converter space, and although it may be possible to preserve uniform and approximately spherical packing in fine-grained material, yet, the increased skin friction caused by the great extension of surface to which the reactants are exposed during their passage, raises the value of the frictional loss or back pressure in the converter to such a high figure as to preclude economic working A second objection of a practical nature to undue

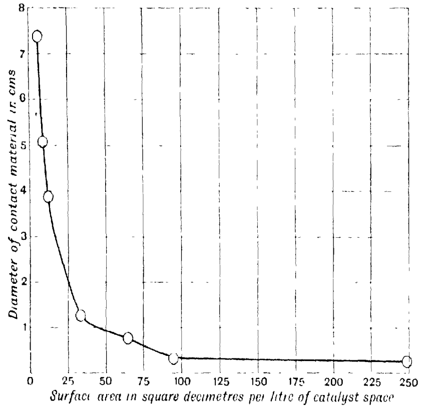


FIG 5

reduction in catalyst size may be raised in that even coarse powders are very prone to removal by passage of the gaseous reactants, and are liable to exhibit the phenomenon of "channel formation" due to slight unevenness in the distribution of the material.

Types of apparatus for experimental work.—For the experimental investigation of catalytic processes involving gas reactions at a solid contact substance, two simple types of apparatus may be described which have proved of great utility.

Sabatier developed a form of apparatus which has been used with success in the investigations which he has conducted with his collaborators on the hydrogenation of organic liquids This type of apparatus is generally applicable to the study of catalytic interaction of gases and of vapours of liquids.

A glass, or preferably quartz, tube of suitable dimensions forms the reaction space, in which is placed a layer of the catalytic agent to be employed in the case of nickel a layer of the unreduced oxide.

One end of the tube is closed with a stopper carrying two tubes, as illustrated in the accompanying diagram (Fig 6), of which one serves as delivery tube for the incoming gas (hydrogen in the case of hydrogenation studies), the other for delivery

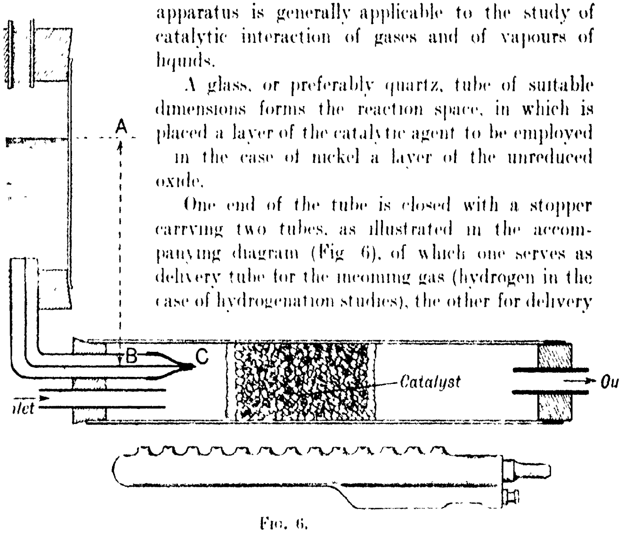


FIG. 6.

f the liquid, or of the gas to be investigated In the case of liquids capillary tube is employed, the liquid being stored in the vertical be *T* The rate of flow of liquid may be regulated by varying the ameter of the capillary and the height of liquid in the reservoir. batier recommends that the inflow of liquid into the reaction space constant by arranging that it does not leave the capillary in drops. y allowing the end of the capillary *C* to touch the inside of the action tube this may be readily attained. If the reservoir *T* be nnected with a vessel of considerable dimensions the height of uid, *AB*, may be maintained reasonably constant over long periods.

The reaction tube is heated in any suitable manner, either by gas me, as in an organic elementary analysis, or more conveniently for the attainment of an even temperature, by means of an electric resistance furnace. In the latter case, where the heating is uniform around the tube, the catalyst may be inserted as a plug in the reaction space as alternative to the layer of material employed in the gas-heated tube. The heating should extend sufficiently far along the tube to allow of vaporisation of the incoming liquid at C[1]

With sufficiently volatile liquids, an alternative arrangement is possible in which the mixture of the gas and vapour is obtained by llowing the former to bubble through the liquid, passing thence lirect into the reaction space. By regulation of the temperature of the iquid and by ensuring saturation of the gas at the given temperature, from a knowledge of the vapour pressures of the liquid, a definite ratio of gas to vapour may be readily attained. The authors have found this is a suitable method of introducing definite quantities of steam and alcohol vapours into the reaction mixture It has been found, however, advisable in the case of steam, first to supersaturate the gas with steam by passage through water maintained at a temperature higher than that required to give the definite ratio, and then to pass the supersaturated gas through a further quantity of water maintained at the requisite temperature

Sabatier, in the case of solids which are readily vaporised, places the material in porcelain boats inside the reaction space some distance before the catalyst mass The incoming gas carries along with it the vapours of the solid arising from the heated boats

The temperature employed may be determined according to Sabatier by means of a thermometer placed alongside the reaction tube, when the latter is embedded for evenness of temperature distribution in a layer of heated magnesia or fine sand. Alternatively, it may be placed inside the reaction vessel, in which case, however, there is difficulty in altering its position to determine the temperature at various points With the latter alternative, a thermo-couple is more useful than a mercury thermometer, owing to the difficulty of reading the latter when inside the tube.

A modified form of apparatus can be conveniently used, more especially for the investigation of catalytic gas reactions at different temperatures. The features of the apparatus are its simplicity and adaptability, ease of temperature control and observation, as well as evenness of temperature distribution. The accompanying diagram (Fig. 7) illustrates the salient details of the apparatus The outside glass or silica tube is electrically heated by means of a resistance wire suitably insulated and lagged. The upper end of the tube terminates in a length of tubing of narrower bore sufficient to pass the thermometer or thermo-couple, which may be adjusted in position at any suitable height. The catalytic material is contained in an inner concentric tube which, when in position, allows of a narrow space between the inside of the heater tube and the outside of the catalyst tube, through which the gases pass up from below and are thus brought to the desired temperature. By this arrangement, apart from the radiation across

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[1] Other modifications of this apparatus are described by Taylor and Neville, *J. Amer. Chem. Soc.*, 1921, **43**, 2060, Adkins, *ibid.*, 1922, **44**, 2177, Adkins and Nissen, *ibid*, 1924, **46**, 139.

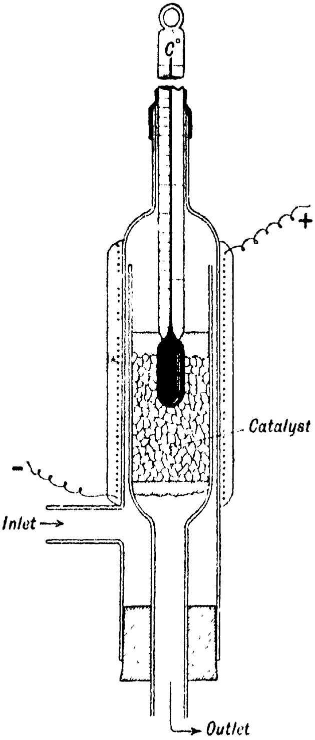

FIG. 7.

the gas space, the heating of the catalyst material is caused by the incoming gases, and so can be the more easily regulated. Also, the charging of the reaction space with the contact body is more readily effected than in the apparatus designed by Sabatier. Large sizes of this type of catalyst furnace, constructed in iron with suitable modifications, have been employed with considerable success in experiments upon a semi-technical scale.

CHAPTER V

PROMOTERS, MIXED, SUPPORTED, AND PROTECTED CATALYSTS

THE positive catalytic effect produced by a given substance in a given reaction may, it is found, be considerably enhanced by the admixture with the catalyst of small quantities of other substances. Normally, the acceleration produced by a catalyst is proportional to the concentration of the catalytic agent present, as will be illustrated in numerous examples in the following pages; in the case of two catalysts accelerating the same reaction, their double effect is frequently the same as if each were reacting singly. This is true, for example, when a mixture of colloidal platinum and gold takes part in the decomposition of hydrogen peroxide. But exceptions to this rule are common. Mercury and copper sulphates each accelerate the oxidation of aniline or naphthalene by concentrated sulphuric acid. Their joint effect is greater than the sum of their individual activities. More especially, however, in gas reactions accelerated by solid catalysts does the phenomenon referred to become pronounced. The modification of catalytic activity produced by even minute quantities of foreign materials is in many cases quite astonishing, and exploitation of this factor has been most marked in recent practical applications of catalysis. This may be illustrated by a textual quotation from the Badische Company's English patent[1] on improvements in the manufacture of hydrogen by the water-gas-steam catalytic process.

"In the researches on the production of hydrogen from mixtures of carbon monoxide and steam, according to the equation

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

we have found that the power of catalytic agents generally can be improved by the presence of certain bodies which may be termed promoters. We have found, for instance, that the activity of the catalytic agents, especially those consisting of or containing iron, nickel or cobalt, or oxides thereof, and also the catalytic activity of other metals or oxides even such as, by themselves, are less active, can be greatly increased by the addition of certain compounds or bodies to which, as aforesaid, may be given the name promoters. Thus the activity of catalytic agents consisting of or containing iron, nickel or cobalt, or oxides thereof, can be greatly increased by the addition of oxygen compounds of chromium, thorium, uranium, beryllium, antimony, and the like. Further, a catalytic agent consisting of or containing iron in admixture with less than its weight of nickel, particularly after working for a long time, yields better results than does either iron or nickel when employed by itself. . . . In many cases, particularly when using catalysts of weak activity, we prefer to employ as promoter a compound which differs considerably from the catalytic agent, in particular with respect to valency, chemical basicity, and capability of reduction . . The contact masses containing iron as the catalyst agent, and a smaller quantity of nickel, as above described, as promoter, bring about rapid and far-reaching conversion without the simultaneous formation of methane, even when a comparatively low temperature is employed, and, as compared with pure nickel, are further characterised (especially when suitable oxides or oxy-compounds are employed as binding agents, or as promoters) by possessing greater stability and less sensitiveness to deleterious influences such as, for instance, fortuitous increase of temperature and impurities in the gas mixture "

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[1] No. 27963/1913.

As examples of such contact masses the patent application contains, *inter alia*, the following .

(1) The mixture obtained by evaporation and ignition of a solution of 85 parts of iron nitrate and 15 parts of chromium nitrate.

(2) The mixture obtained by ignition from a solution of the ingredients: 40 parts of ferric nitrate, 5 parts of nickel nitrate, and 5 parts of chromium nitrate

(3) A preparation obtained by solution, evaporation and ignition of 194 parts of iron nitrate, 5 parts of ammonium bichromate, and 1 part of thorium nitrate

Especially in this latter case is the principle of promoter action illustrated. It is clear from this example that a mixture containing, in the main, oxide of iron with admixture of but 2·5 per cent of chromium compounds and only 0·5 per cent of ceria, is claimed to have considerable superiority as catalyst over a contact mass containing iron oxide alone.

In addition to the use of promoted and mixed catalysts, consideration must also be given to the use of catalysts spread upon suitable supports. Stress has already been laid on the relation between physical condition and catalytic activity. Experiment has shown that efficient distribution of catalyst material may be secured by spreading the material upon an inactive support, economy of catalyst thereby resulting. The classical example is the use of finely divided platinum in the form of platinised asbestos or as platinised magnesium sulphate in the contact process of sulphuric acid manufacture. In view of the phenomena occurring in the use of promoters and of mixe catalysts, it is possible that similar advantageous results accrue fro the use of support materials, which are not to be explained from th point of view of distribution of catalyst alone. It is for this reaso that the three classes of catalysts, promoted, supported, and mixe are here grouped together for discussion.

PROMOTER ACTION

Information on the subject of promoter action is widely scattered through the literature and is in general meagre, being largely limited, in the field of heterogeneous catalysis, to simple statements in patent specifications that certain substances are able to activate some particular catalyst Pease and Taylor[1] collected the major portion of this literature with the object of increasing interest in the investigation of this field. Their compilation has been followed by a number of communications, from various sources, dealing more especially with the mechanism of particular catalytic reactions The results will be set forth in detail in subsequent paragraphs

The definition of promoter action.—In attempting a definition of promoter action, Pease and Taylor construed the phenomenon very broadly and included *all those cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the supposition that each substance in the mixture acts independently and in proportion to the amount present.* The breadth of this definition, while useful for purposes of literature compilation, has obvious defects It is apparent that, within the scope of this definition, cases of promoter action, of mixed catalysts and of supported catalysts, may all be included Furthermore, from what has preceded in reference to the relation of activity to distribution, it is apparent that the *amount* of a catalyst present is no correct measure of catalytic effect as witnessed by the extreme variability in catalytic activity per unit area of metallic foil and metallic mirrors noted by Hinshelwood, Hartley and Topley[2] To define the field more particularly Pease and Taylor suggested the use of the terms "activation" and "co-activation", the former to designate the activation of a catalyst by a substance relatively inert catalytically, or by a small quantity of a relatively active substance The co-activation of a number of catalysts each by the rest would obviously be a case which we have here designated as that of a mixed catalyst.

As far as a study of the literature has revealed, the term "promoter" was first applied in the patents of the Badische Anilin- und Soda-Fabrik[3] on ammonia synthesis to the substances themselves inert catalytically, which are able to increase the activity of a moderately good catal by admixture in small quantity with it. It can be maintained with some degree of success that the deliberate admixture of inert materials in small amounts with catalytic agents to improve the efficiency of the catalyst constituted a novel advance in the technique of contact catalysis. It is also certain, however, that this enhancement of activity had been achieved, unconsciously, many times previous to the deliberate use of such added agents. Indeed, as will later be shown, evidence as to the mechanism of the effect produced by such additions was obtained many years previously by Baxter in an investigation in no way connected with the problem of catalysis (see p. 107). The conscious development of this aspect of the subject by the Badische Company is well attested, however, by the patents covering a wide variety of catalytic processes in which the efficacious use of promoters was claimed. In addition to those already mentioned, the following may be cited. Thus, in hydrogenation processes, claim was made[1] for the use of iron, nickel, cobalt, or copper as catalysts, improved by addition of one or more of the following—often in quantities of less than 1 per cent: oxides or oxygen containing salts of the alkaline or rare-earth metals, or beryllium, manganese, magnesium, uranium, vanadium, nobium, tantalum, chromium, titanium, or boron, or difficultly soluble phosphates, tungstates, or selenates of the alkaline earths (or lithium), or compounds of fluorine, tellurium, or antimony, or the elementary tellurium or antimony. For the reduction of nitro-aromatic compounds, another patent[2] states that the copper used as catalyst may be considerably improved by the addition of zinc, silver, magnesium oxide, alumina, or sodium silicate. Other Badische patents[3] deal with the promotion of catalysts for use in the oxidation of ammonia. Iron oxide admixed with small amounts of bismuth oxide or with a mixture of bismuth and cerium oxides are examples of this class.

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[1] *J. Physical Chem.*, 1920, **24**, 241.

[2] *Proc. Roy Soc.*, 1922, **100A**, 575

[3] B.P 19249, 16/8/10.

In their development of the field of promoted catalysts, with a view to patent protection, it is evident that the Badische Company attempted to extend the concept of a promoted catalyst to include cases which more particularly belong to the category of mixed catalysts. Thus, in ammonia synthesis, claims were made[4] for the use of mixtures of metals or their compounds from different groups or sub-groups of the periodic table. Another[5] claims the use of a catalyst which shall consist of one substance capable of absorbing hydrogen and another capable of absorbing nitrogen, palladium-molybdenum being cited as a catalyst. The inclusion of a 50-50 iron-molybdenum catalyst in a promoted catalyst patent clearly indicates the effort to include such cases of mixed catalysts in the general category of promoted patents. Such inclusions undoubtedly weaken any claim which the Badische Company might make to protection for promoted catalysts, since there is an abundance of examples in the prior art of the superiority of mixed catalysts over either constituent singly. Thus in the case of ammonia synthesis itself, an Austrian patent granted to Hlavati[1] claims the use as catalyst of a mixture of titanium or titaniferous bodies in admixture with platinum. A French patent[2] to the Christiania Mine Kompanie claims titanium in a finely divided condition on neutral supports *with or without the addition to the titanium of platinum or the platinum metals. Further, the titanium could be replaced by bismuth, antimony, or alkali or alkaline earth* metals, provided that platinum or the platinum metals were employed. The use of metallic couples as reducing agents[3] is a very old example of the mixed metals possessing an activity when together much greater than the combined effect of each singly. In the case of the zinc-copper couple the reaction is not generally regarded as catalytic because the zinc reacts; but it is catalytic as regards the copper. Cohen and Dakin[4] report the catalytic action of an aluminium-mercury couple in the halogenation of benzene, toluene, and xylene. They state that the fragments of the couple remain unchanged during the reaction. These examples may be taken as typical. Other cases, more especially those of mixed catalysts in homogeneous systems, will be discussed at a later stage.

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[1] D.R.P. 282782, 12/12/13; B.P. 2306, 28/1/14.

[2] B.P. 5692, 15/4/15.

[3] D.R.P. 283824, 14/4/14, 287009, 24/5/14; B.P. 13848, 18/6/14.

[4] B.P. 26167, 14/12/11.

[5] B.P. 21151, 25/9/11.

It would seem desirable, therefore, to restrict the term "promoter action" to the beneficial effect produced in a catalytic agent by admixture with a relatively small quantity of a material, inert or of negligible catalytic activity in the reaction in question. The higher activity obtained by using several catalysts mixed, over that obtained when they are employed separately, would then be a case of "co-activation." At the other extreme, the disposition of an active catalyst on a relatively large quantity of an inert or practically inert support material may be regarded as the production of a supported catalyst. It is very evident that the three classes will merge together, and no decisive line of demarcation between them can be drawn. It may be found also that the basis of the enhanced activity produced in all three types of product may, in certain cases, be the same. In other cases a marked differentiation of mechanism will be established.

Examples of promoter action.—Ipatiew appears to have been among the first to record in detail promoter action in a heterogeneous system. He found[5] that in the presence of copper oxide, and in a *copper* tube, amylene was only one-third converted into isopentane by hydrogen at 200 atmos. at a temperature of 300° C. in twenty-eight hours; with copper oxide in an *iron* tube complete conversion was effected in twelve hours under the same conditions. The same relation holds also for the hydrogenation of tetrahydrobenzene, tetrahydrotoluene, pinene, and carvene

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[1] Austr. P. 45/2938, 1895.

[2] F. P. 225183, 1896.

[3] Gladstone and Tribe, *Proc. Roy. Soc.*, 1872, **20**, 218; *J. Chem. Soc.*, 1872, **25**, 461; 1873, **26**, 445, 453, 678, 961; 1874, **27**, 208, 406, 615; 1875, **28**, 508; 1876, **30**, 37; 1877, **31**, 561; 1878, **33**, 139, 306; 1879, **35**, 107, 172, 567; Williams, *Analyst*, 1881, **6**, 36; Ulsch, *Zeitsch. anal. Chem.*, 1891, **30**, 175; Thorpe and Eccles, *J. Chem. Soc.*, 1873, **26**, 541; Bothamley and Thompson, *J. Chem. Soc.*, 1888, **53**, 164; Muller and Wegelin, *Zeitsch. anal. Chem.*, 1911, **50**, 615; Harcourt, *J. Chem. Soc.*, 1862, **15**, 385; 1863, **16**, 289; Devarda, *Chem. Zeit.*, 1892, **16**, 1952.

[4] *J. Chem. Soc.*, 1899, **75**, 893; 1907, **79**, 1111.

[5] *Ber.*, 1910, **43**, 3387.

Ipatiew also records [1] an interesting case in which a hydrogenation and dehydration catalyst appear each to activate the other when used together to carry out a reaction which ordinarily would involve several successive steps He found that camphor was hydrogenated in presence of nickel oxide at 320°-350° C., yielding borneol. This in turn could be dehydrated by alumina at 350°-360° C., yielding camphene, which could then be easily hydrogenated at 240° C. to give camphene. By using a mixture of nickel oxide and alumina in presence of hydrogen the complete reaction could be effected at a temperature of 200° C. or less. Similarly, fenchone may be hydrogenated at 240° C. to give fenchenol, which, however, can only be dehydrated with difficulty. In presence of a mixed nickel oxide-alumina catalyst, a hydrogenation-dehydration process readily occurs at 215° C., yielding fenchane from the original fenchone.

The extraordinary increase in the light emissivity of thoria incandescent mantles when admixed with 0·9 per cent of ceria has been utilised, as is well known, in the technical development of the Welsbach incandescent mantle. A recent research [2] has established that a maximum in the efficiency of catalytic oxidation of electrolytic gas mixtures occurs at the same concentration of ceria in thoria. Upon this basis, it seems reasonable to assume that the mantle is a catalyst for the oxidation of illuminating gas, the ceria playing the rôle of promoter, more rapid combustion and a higher temperature of the mantle being thereby attained.

In the catalytic oxidation of ammonia, Maxted has obtained [3] curves indicating the relative efficiencies of iron alone and admixed with other metals as promoters. Bismuth, tungsten, and copper enhanced the yield of nitric acid with a given time of contact. Lead, manganese, and calcium diminished the yield. These observations are the basis of patent claims by Maxted and Ridsdale [4] for catalysts for ammonia oxidation.

The Harger-Terry patent [5] for the preferential catalytic combustion of carbon monoxide and oxygen in presence of hydrogen claimed, in addition to simple oxide catalysts, the use of promoted oxide catalysts. An iron catalyst containing 2·5 per cent chromium oxide and 0·5 per cent cerium oxide was found to be superior to an iron oxide catalyst, and operated more efficiently at considerably lower temperatures. The catalytic oxidation of carbon monoxide in air at room temperatures can be achieved by mixed oxide catalysts,[1] of which the most notable is "Hopcalite", a mixture of 60 per cent manganese dioxide with 40 per cent copper oxide This case is of especial interest since it has attracted considerable experimental study with a view to elucidation of the mechanism whereby the mixed catalyst is more efficient than either singly. This work is discussed in detail in the next section.

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[1] *Ber.*, 1910, **43** 3387.

[2] Swan, *J. Chem. Soc.*, 1924, **125**, 780.

[3] *J. Soc. Chem. Ind.*, 1917, **36**, 777

[4] B.P. 10781/1915, 126083/1916.

[5] B.P. 127609/1917.

The mechanism of promoter action.—One case in which the mechanism of promoter action seems definitely to have been ascertained is available in the older literature. Elissafoff studied[2] the action of glass wool and heavy metal salts on the velocity of decomposition of hydrogen peroxide both singly and in conjunction with each other. Elissafoff showed that, together, the glass wool and heavy metal salt effected a much more rapid decomposition of the peroxide than would be anticipated on the basis of additive effects. Thus, with a decomposition velocity of 0·86 in presence of 0 5 grm glass wool in 20 c c of peroxide, and one of 1·63 in presence of 1·54 millimolar solution of copper sulphate without glass wool, a solution with the same copper sulphate concentration plus 0·5 grm glass wool in 20 c c gave a decomposition velocity of 10·8; all the velocity units are expressed in arbitrary units The concentration of hydrogen peroxide was 12 millimolar. In this case at least the mechanism is apparent It is known that the decomposition of peroxide takes place at the glass surfaces It was probable that the copper salt was concentrated at the glass surface and so exercised greater effect That this was so the following observations indicate clearly The unimolecular constants for two copper ion concentrations of 1 and 10 millimols per litre were 0·0013 and 0·0023 respectively, in the ratio, therefore, of 1 1·77 The amounts of copper salt adsorbed from these solutions by Jena glass powder of the same glass were in the ratio of 1 1·73 It is apparent that the decomposition velocities are proportional to the amounts of adsorbed copper salt This case is certainly, therefore, a reaction velocity at the surface and not a diffusion velocity. Were it possible to make adsorption measurements, other modes of decomposition of hydrogen peroxide would possibly be found to be of the same type.

Hydrogenation processes—An informing contribution to the theory of promoter action has been made by Medsforth,[3] who has studied the effect of promoters added to a nickel catalyst in the hydrogenation of carbon monoxide and carbon dioxide to yield methane. Reasoning from the simultaneous production of water in the reaction, the addition of catalytic dehydrating agents to the nickel catalyst was made with material increase in the attainable reaction velocity for a given conversion of the reactants Ceria, thoria, glucina, chromium oxide, alumina, and silica gave an, from seventeenfold to twelvefold, increase in velocity over that obtainable with the straight nickel catalyst. Zirconia, molybdenum oxide, and vanadium oxide were somewhat less efficient, though still good, promoters. Tin and magnesium oxides, copper and silver metals, produced no acceleration over the straight nickel. With the carbon dioxide reaction the increases in velocity effected were somewhat less than those recorded for the monoxide reaction above. The order of efficiency was exactly the same. The order of efficiency is roughly that of oxide catalysts recorded by Sabatier in reference to strict dehydration processes.

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[1] Lamb, Bray, and Frazer, *J Ind Eng Chem*, 1920, **12**, 217.

[2] *Zeitsch Elektrochem*, 1915, **21**, 352.

[3] *J. Chem. Soc.*, 1923, **123**, 1452.

In explanation of the activity of the promoters, Medsforth assumes the function of the nickel to be to assist the union of the gases to form a " complex " or intermediate compound of the methyl alcohol type, probably via formaldehyde. The promoter then functions as a catalytic dehydrating agent on the intermediate compound giving water and a methylene radical, whence, immediately, methane results. The promoter assists the known dehydrating action of the nickel. This can be schematised thus:

$$CO+2H_2 \longrightarrow H_3C.OH \longrightarrow \rangle CH_2+H_2O.$$

The combined dehydrogenation and dehydration effected by Ipatiew[1] with a nickel alumina catalyst, whereby the conversion of camphor to isocamphene is effected at 200° C. in one step, is cited as supporting evidence.

Medsforth calls attention to an important feature of promoter action which he has noted, that of *selective promotion*. It would appear that when two reactions, both capable of being accelerated, take place at the same time in the presence of the same catalyst and the same promoter, that which is normally slower is accelerated to a greater comparative degree than that which is normally the faster. Support for this statement was obtained in the observation that when carbon monoxide and steam react in the presence of nickel and nickel promoters, whilst carbon dioxide and hydrogen are the main products, methane is also formed, the quantity of which is greater when, for example, alumina is present than when nickel alone is used. Similarly, in the production of methane from carbon monoxide and hydrogen, more carbon dioxide is formed as a by-product due to the simultaneously occurring water-gas reaction, when promoters are added to the nickel catalyst, than if this latter is used alone.

In discussing the applications of this dehydration hypothesis Medsforth reviews several cases of promoter action. For catalysis of the water-gas reaction with iron oxide as catalyst, it is significant that the promoters among the most effective are hydrating agents and oxygen carriers. The action of ceria-thoria in the incandescent mantle may also be in part due to combined oxygen carrier-dehydration effectiveness.

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[1] *J. Russ. Phys. Chem. Soc.*, 1912, 44, 1695.

As a temporary classification of promoters for purposes of discussion Medsforth gives the following

(1) The promoter decomposes intermediate compounds formed by the catalyst

(2) The promoter causes the reacting substances to combine, the resulting intermediate compound being decomposed by the catalyst

(3) The promoter adsorbs or combines with one of the reacting substances producing a greater concentration of the latter at the catalyst surface

The origin of the carbon dioxide in the methanation process has been elucidated by Armstrong and Hilditch,[1] who have shown that when purified water gas is passed over nickel at 200°-300° C the predominating reaction is $2CO + 2H_2 = CO_2 + CH_4$ The reaction is regarded as the sum of two reactions

$$CO + H_2O = CO_2 + H_2,$$
$$CO_2 + 2H_2 + 2H_2 = CH_4 + 2H_2O,$$

the former of which is regarded as occurring in the same manner as the reaction in presence of copper previously studied by them,[2] namely, via formic acid, $CO + H_2O \rightarrow HCOOH \rightarrow H_2 + CO_2$ With cobalt the reaction commences at a lower temperature, 180° C, but the above reaction is subsidiary to the main methanation process, $CO + 3H_2 = CH_4 + H_2O$ Silver is inert, iron almost so, platinum and palladium of minor activity Mixed catalysts were less efficient than the single catalyst With nickel at increasing pressures up to 6 atmospheres the minimum temperature of interaction rises The reaction yielding carbon dioxide and methane produces more methane from water gas than any of the other reactions It may, therefore, have value as a means of increasing methane content or lowering carbon monoxide content of town's gas The authors state that $CO_2 + H_2$ goes directly to methane and gives no carbon monoxide, so that partial reduction is apparently not taking place This is at variance with some observations made in the laboratories of the Munitions Inventions Department in England, during the war, where methane prepared from carbon dioxide and hydrogen contained a small percentage of carbon monoxide

In contrast to the conclusions of Medsforth cited above Armstrong and Hilditch[3] conclude, with regard to the "promotion" of a straight hydrogenation process, the simple addition of hydrogen at an unsaturated linkage, in presence of nickel, alumina, silica, oxides of iron and magnesium being employed as promoters, that the stimulation observed can be satisfactorily explained on the basis of increased available catalytic surface of the nickel There is some evidence of the removal or adsorption of catalyst poisons (sulphates in the precipitated oxides, or traces of impurities in the oil hydrogenated);

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[1] *Proc Roy Soc.*, 1923, **103A**, 25

[2] *Proc Roy Soc*, 1920, **97A**, 265

[3] *Proc Roy Soc*, 1923, **103A**, 586

but these appear as minor influences compared to the effect on the extent of surface of nickel produced. They have been able to make an appreciably less amount of reduced nickel effect the same amount of action whatever the extent of the catalyst in alumina or other "promoting" oxide.

Armstrong and Hilditch[1] showed that the presence of sodium carbonate effectively promotes the hydrogenation of phenol at nickel surfaces. About 25 per cent by weight of nickel appears to give the maximum effect. In the presence of carbonate the reaction rate is more nearly linear than in the absence of the carbonate. This factor suggests that the function of the promoter is a protective one to the catalyst, keeping it free of inhibiting impurities.

Oxidation processes.—For the rôle of ceria in promoting the reaction between gases in ceria-thoria catalysed combustions, Swan concludes[2] that there are at least two possible explanations:

(1) The ceria behaves as an oxygen carrier during the combustion of the gases.

(2) The ceria, by increasing the electron emission of the thoria, causes a greater ionisation of the gases and more efficient combination.

This latter explanation could be experimentally tested.

Adsorption and the mechanism of promoter action. In a research on the atomic weights of cobalt and nickel, Baxter investigated[3] the occlusion of hydrogen by the reduced metals and reached conclusions which are of fundamental importance in the study of catalytic action in general and promoter action in particular. Baxter found that the finely divided metals obtained by reduction of the oxides in hydrogen gas occluded relatively large amounts of the gas. He found that the volume of occluded hydrogen varies, in the case of the metal reduced from the oxide, with its purity and the temperature of reduction. The latter fact is of significance in the general problem of adsorption and catalysis, and, as such, has already been discussed in a preceding chapter. The former fact, the influence of impurities, has a marked bearing on the problem of the mechanism of promoter action. Baxter found that ordinary "chemically pure" oxide yielded a metal on reduction which occluded very considerably more hydrogen than oxide which may be designated of "atomic weight purity". Having traced the co-ordination between extent of surface and occluding power Baxter concludes that when impurities, for example, silica, are present in the oxide, the resulting metal is less compact than that obtained by identical treatment from the atomic weight purity oxide. In other words, a pure metal sinters more readily than a metal obtained by reduction of an oxide containing certain impurities. The fact that it is extent of surface which counts, cobalt ingots being known to occlude practically no hydrogen, makes it certain that the phenomenon designated by Baxter as occlusion is, for the most part, what is now known as surface adsorption of the gas. A further fact of significance was Baxter's observation that the metal obtained by reduction of cobalt bromide occluded practically no hydrogen, and the presence of sodium bromide had no influence on the amount occluded. In other words, not all impurities present in the substance undergoing reduction are effective in promoting extension of metal surface

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[1] *Proc. Roy. Soc.*, 1922, **102A**, 21.

[2] *J. Chem. Soc.*, 1924, **125**, 784.

[3] *Amer. Chem. J.*, 1899, **22**, 351.

Applied to the problem of the mechanism of promoter action, the experimental observations of Baxter obtained for quite different purposes may be summarised thus (1) The presence of impurities in the materials from which catalytic metals are prepared may increase considerably the extent of adsorbing surface and, therefore, in agreement with earlier observations in a preceding chapter, may increase catalytic activity of the reduced metal, (2) certain impurities, for example, silica, are much more efficient than others, for example, sodium bromide, in producing extended surface. In these two observations we have two factors fundamental to the problem of promoter action, actual increase, by an added promoter, of the catalyst surface and specificity of promoting agent, the specificity being associated with the influence of the added agent on extent and nature of surface Such studies must be multiplied by the student of catalysis with deliberate rather than accidental inclusions in the materials studied

Two such cases have already been studied, one by Hurst and Rideal,[1] on adsorption of carbon monoxide and hydrogen, the other by Taylor and Russell [2] In the latter work, measurements of adsorption by nickel obtained by reduction of the oxide, and of nickel-thoria from the oxide containing thoria as a promoter, have been made Adsorptions of hydrogen and carbon dioxide were measured, since the researches of Medsforth already cited showed that the reactivity of these gases was much enhanced by the use of a nickel catalyst promoted by thoria The experimental work shows that no proportionate increase in adsorption accompanies the activity shown by the promoted catalyst The surface has therefore undergone a qualitative rather than a quantitative change Whereas the promoted catalyst effects a tenfold increase in velocity over the non-promoted catalyst, the extension of surface, as measured by adsorption of either the carbon dioxide or the hydrogen at reaction temperature, only undergoes a 20 per cent increase This is in harmony with the view of a composite catalyst surface with localised active centres Even if it be assumed that the whole of the nickel surface capable of adsorbing hydrogen were catalytically active in the case of the promoted catalyst, it would follow that not more than 10-12 per cent of the surface of the unpromoted catalyst surface adsorbing hydrogen would have any catalytic activity. Hurst and Rideal's results are discussed in the succeeding section.

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[1] *J Chem. Soc*, 1924, **125**, 694-705

[2] *Dissertation*, Princeton, 1924, *J Phys Chem*, 1925, **29**, 1325

One function of promoter action was suggested in the previous edition of this book (p. 31), in reference to the use of mixed catalysts for ammonia synthesis. It led to the conclusion that the original iron tended to adsorb or form a loose compound with a greater proportion of hydrogen to nitrogen than required by the stoichiometric ratio. The admixed catalysts, being in the main nitride-forming metals, for example molybdenum, would promote a more favourable hydrogen-nitrogen ratio. Bancroft extended this idea,[1] suggesting that the catalytic agent activates one constituent of the reaction chiefly and that the promoter activates the other. Some measure of activation will be necessary before such a conclusion can be experimentally tested. Experimental work on ammonia synthesis catalysts has not confirmed this point of view, thus simply outlined, but there is still no proved theory of mechanism in the ammonia synthesis reaction.

Interface phenomena and the mechanism of promoter action.—There are many places in the chemical literature which exemplify the statement that the molecules at the boundary between two phases are in a peculiarly labile or active state. Faraday observed that a perfect crystal of sodium carbonate or sodium sulphate refuses to effloresce until the surface is scratched or broken. He also observed that the efflorescence spreads from the injured place. Crystals of hydrated cadmium sulphate show this behaviour remarkably well. They are readily obtained in large and perfect form, which maintain a constant weight in a desiccated space until a boundary between a hydrated and a dehydrated phase is established. Langmuir[2] has shown that, in the dissociation of calcium carbonate by heat, the carbon dioxide is produced only at the boundary between the carbonate and oxide phases. The dissociation of silver oxide into its elementary constituents, studied by G. N. Lewis,[3] is a parallel case, Lewis observing that the rate of dissociation increased with increasing production of silver. Silver was termed the autocatalyst of the reaction. Reactions of this type occurring at an interface are necessarily characterised by an auto-accelerated reaction rate, since, initially, there is little or no interface at which reaction can occur, and, with increasing reaction, an ever increasing region of interface is produced. The different nature of the dissociation process when such interfaces are not set up is well illustrated in the case of mercuric oxide dissociation studied by Hulett and G. B. Taylor.[4] In this case, at temperatures where dissociation becomes marked, the mercury formed is also vaporised. No interface results and, so, no acceleration of the dissociation is obtained.

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[1] *First Report, Committee on Contact Catalysis*, p. 16, 1922.

[2] *J. Amer. Chem. Soc.*, 1916, **38**, 2263.

[3] *Zeitsch. physikal. Chem.*, 1905, **52**, 310.

[4] *J. Physical Chem.*, 1913, **17**, 567.

As a result, passage of nitrogen gas for twenty-four hours over pure mercuric oxide at 500° C. gave concentrations of oxygen corresponding to only a few millimetres pressure, whereas the true equilibrium pressure at that temperature was upwards of one atmosphere. When interfaces were produced by the addition of foreign substances, iron oxide, manganese dioxide, and platinum, true equilibrium pressures were at once established, measurable both statically and dynamically. The researches of Kendall and Fuchs[1] on the accelerated decomposition of silver oxide, mercuric oxide, and barium peroxide in presence of other oxides is also illustrative of the effect produced by the deliberate creation of interfaces.

In a determination of the dissociation pressure of sodium bicarbonate, Lescœur observed[2] that the development of pressure occurs "slowly at first, then more quickly towards the end. It has seemed to me, moreover, that the final equilibrium was obtained more rapidly the more the proportion of dissociated salt increased." These observations are again characteristic of interface phenomena and are recognised in the technique of dissociation pressure measurements. A mixture of dissociating substance and product is normally introduced into the apparatus in which such measurements are made.

More recently, further evidence of interface phenomena in chemical decompositions is revealed by additional reaction velocity curves autocatalytic in nature. Sieverts and Theberath[3] studied the dissociation of silver permanganate and obtained such a reaction process. Small amounts of impurities increased the velocity of decomposition. Hinshelwood thereupon promptly called Sieverts's attention to his own work[4] upon both inorganic and organic compounds, some cases of which are interface phenomena.

Otto and Fry[5] thought that their results showed the decomposition of potassium chlorate to be a unimolecular process. Any one can see that they are in reality a beautiful example of an auto-accelerated process. Iron oxide promotes the decomposition. Recently[6] they have shown that potassium chloride does the same thing. The presumption is therefore strong that the process is an interface phenomenon. Neville has added[7] to this reaction an interesting case of promoter action. Impure pyrolusite was more effective than pure manganese dioxide. The pyrolusite contained 8 per cent iron oxide. A mixture of 8 per cent iron oxide and 92 per cent pure manganese dioxide had the same efficiency as the impure pyrolusite. The action of the mixture was more than additive of the effects of the two oxides separately, hence the promoter action, elucidation of the mechanism of which was not achieved. It will probably be quite complex.

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[1] *J. Amer. Chem. Soc.*, 1921, **43**, 2017.

[2] *Ann. Chim. Phys.*, 1892, **25**, 430.

[3] *Zeitsch. physikal. Chem.*, 1922, **100**, 463.

[4] *Phil. Mag.*, 1920, **40**, 569; *Proc. Roy. Soc.*, 1921, **99** A, 203; *J. Chem. Soc.*, 1921, **118**, 721.

[5] *J. Amer. Chem. Soc.*, 1923, **45**, 1134.

[6] *J. Amer. Chem. Soc.*, 1924, **46**, 269.

[7] *J. Amer. Chem. Soc.*, 1923, **45**, 2330.

Proof that the enhanced reactivity at an interface was not confined to decomposition processes, but occurred in reactions between solids and gases, was forthcoming in a study by Pease and Taylor[1] of the reduction of copper oxide at moderately low temperatures by hydrogen. It was shown that low temperature reduction of copper oxide granules by hydrogen was negligible until copper nuclei had been established in the oxide mass. Subsequent reaction is then localised at the boundaries between the copper and copper oxide, as can be demonstrated visually by the ever increasing area of the red copper extending outwards from the original nuclei. The form of the curve of reaction rate is typical of an autocatalytic process. It evidently finds its explanation in the higher order of reactivity of an oxide ion adjacent to a neutral atom of copper over that of an oxide ion surrounded on all sides by a copper oxide lattice. Jones and Taylor[2] showed further that the low temperature reduction of copper oxide by carbon monoxide is also an interface phenomenon. Benton and Emmett have recently shown[3] that nickelous oxide reduction by hydrogen is of the interface type, while reduction of ferric oxide, which is known to form solid solutions with the lower oxides, shows a reduction curve which has none of the criteria of the interface type.

Langmuir[4] has pointed out that the hydration of a completely dehydrated substance should show the same auto-acceleration. There seems to be qualitative evidence of this in the dehydration of ethyl alcohol with "over-burnt" lime. In an experiment at room temperature it was found that, for two days, the lumps of lime remained intact in the alcohol. On the third day a small amount of powder appeared alongside the lumps of lime, while treatment for an additional twenty-four hours resulted in the complete disintegration of the lime lumps. Taylor noted[5] the reduction of copper oxide by both hydrogen and carbon monoxide was very pronouncedly retarded by the presence of oxygen in the reducing gas. This is most readily interpreted on the assumption that adsorbed oxygen protects the interface from attack by the reducing gas. The adsorption of oxygen by copper and by copper oxide is known to be small, so that it seems necessary to assume increased adsorptive capacity at an interface to account for the protective action observed.

In a study of the acceleration produced by the presence of oxygen in the union of hydrogen and sulphur, Norrish and Rideal[6] were led to formulate a mechanism for the accelerating action observed. The surface of the liquid sulphur was assumed to consist mainly of S_8 molecules, of which a few were opened and thus polarised. Adsorption of the gases was assumed to occur at the ends of the ruptured

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[1] *J. Amer. Chem. Soc.*, 1921, **43**, 2179; see also Larson and Smith, *J. Amer. Chem. Soc.*, 1925, **47**, 346.

[2] *J. Physical Chem.*, 1923, **27**, 623.

[3] *J. Amer. Chem. Soc.*, 1924, **46**, 2728.

[4] *J. Amer. Chem. Soc.*, 1916, **38**, 2263.

[5] *J. Franklin Inst.*, 1922, **197**, 23.

[6] *J. Chem. Soc.*, 1923, **123**, 1689.

molecule. A strong attraction of the oxygen for the sulphur at one end of the chain, causing a weakening of the sulphur atom at the other end, would result in a more ready combination of such a sulphur atom with hydrogen

Hurst and Rideal[1] applied the concept of interface activity to the problem of promoter action in processes of selective combustion. If a copper catalyst be promoted with small quantities of palladium and the ratio carbon monoxide to hydrogen determined for a series of such promoted catalysts, one of the following results may be anticipated. If the palladium causes no specific effect beyond a surface extension, the ratio CO/H_2 consumed will remain unaltered, alternatively, if promoting action is in reality an additive effect, then the CO/H_2 ratio will decrease with increasing palladium concentration, and the ratio should be capable of accurate calculation from both the known ratios of CO/H_2 for the copper and the palladium each in the pure state and from the stoichiometric composition of the catalyst If, on the other hand, the addition of small quantities of palladium promotes the activity of the oxidised copper for carbon monoxide, we should anticipate a higher CO/H_2 ratio for small additions of palladium, rising to a maximum with subsequent increase in the palladium concentration, and finally falling to a CO/H_2 ratio higher than that for pure palladium at those concentrations where addition of copper promotes the palladium

Hurst and Rideal found that small quantities of palladium, up to 1 70 per cent, increase the ratio of CO/H_2 burnt at any particular temperature in presence of a copper catalyst A maximum occurs on the addition of 0·20 per cent A promoted catalyst containing 1·70 per cent of palladium yields the same ratio as pure copper Catalysts containing more than 1·70 per cent palladium yield a lower CO/H_2 ratio than copper, but higher than palladium This increase in the ratio of CO/H_2 burnt on addition of small amounts of palladium is contrary to that which would be expected, as outlined in the preceding paragraph, either on the basis of extension of surface or the dilution of the catalyst surface with palladium The result obtained is to be anticipated, however, if the reactivity of the oxidised coppe at junctions such as Cu Pd is affected

To elucidate further the mechanism of the promoter action, Hurs and Rideal[2] studied the adsorption of hydrogen and carbon monoxid singly and in various mixtures on copper, palladium, and promote catalysts They conclude that the addition of palladium to coppe produces an increase in the carbon monoxide adsorption and a decreas in the hydrogen adsorption, as well as a relative increase in the carbo monoxide of the adsorbed phase in the presence of both gases Th relative increase in the adsorption of carbon monoxide was found o be in good agreement with the relative increase in the ratio CO/H onsumed in the catalytic combustion process The specificity o the effect on adsorption produced by the palladium promoter is further evidence that the promoter action is not merely due to surface extension but involves the further factor of the nature of the interface between catalyst and promoter.

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[1] *J Chem Soc.*, 1924, **125**, 685.

[2] *J Chem. Soc*, 1924, **125**, 694

Promoter action and concentration.—It may be anticipated that much useful information with regard to the mechanism of promoter action and to the nature of catalyst surfaces will result from a knowledge of the relationship between extent of promoter action and the concentration of promoter used. As yet, the quantitative evidence accumulated on this point is very meagre. Most of the statements concerning promoter action by added substances have no information which would indicate what the optimum concentration of promoter is for the given reaction.

The most comprehensive data on this point are contained in the contribution of Medsforth[1] already discussed. Medsforth studied the efficiency of promoter action in the synthesis of methane from carbon monoxide and hydrogen with nickel and nickel-promoted catalysts spread on pumice support, by ascertaining the maximum speed of gas passage over a given quantity of catalyst at which a given degree of conversion could be achieved. With nickel catalysts alone on pumice the desired conversion was achieved at a speed of 32-35 c.c. per minute. In the following table are recorded the speeds with which the same conversion is attained with various promoted nickel catalysts at various concentrations of promoter in the nickel catalyst.

Medsforth concludes that the tabulated results show no relationship between the molecular weight of a promoter and its optimum concentration. Some slight tendency, however, can be observed. With beryllium oxide the optimum concentration is around 20 per cent. With alumina this occurs at 15 per cent. Medsforth calls particular attention to the flatness of the curve of speed against promoter concentration once the optimum concentration has been passed. Thus, in the case of ceria, the range from 3 to 15 per cent promoter shows no variation in permissible speed of gas passage greater than the experimental error, although the promoter concentration varies five-fold. In discussing this feature, Medsforth distinguishes two cases, the one in which catalyst and promoter are deposited on a support, uniform distribution being assumed, the other in which the catalyst is deposited on the promoter.

As an example of the former, Medsforth discusses a nickel-thoria catalyst, with an optimum promoter concentration amounting to 10-12 per cent Ni by weight. From the relative weights of nickel and thoria, it is calculable that at the optimum concentration the surface of the promoter is approximately one-fortieth of the catalyst. An additional 1 per cent of thoria only increases the promoter surface an additional one-four-hundredth With thoria present equal in weight to the weight of nickel the promoter surface is only one-fourth *to one-fifth of the total Hence, it may be concluded that around the*

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[1] *J. Chem. Soc.*, 1923, **123**.

Promoter Per cent of Ni	Maximum Speed in c c /min						
	Ce_2O_3	ThO_2	GlO	Al_2O_3	Mo_2O_3	V_2O_3	Cu
0·5	300	60	32	75	32	32	33
1	540	320	35	200	40	54	30
2	560	420		260		60	
3	590						
4	620						
5	610	480	160	320	80	95	
6						120	
7	600					140	
8		590				120	
10	600	600	290	450	200	110	26
12		600		470	220		
15	580	600		500	190		
16				490			
18			540				
20	560		580	460			
23			560				
50	470	570	420	380	110	24	
100		530	280				No action
200	380	470					
About 400		350					

optimum concentration marked changes in velocity with change in concentration of promoter would not be expected Medsforth's data conform to this conclusion

In the case of a catalyst deposited on a promoter the conditions are different If it be assumed that 5 grms of thoria can take up on its surface 0 1 grm of nickel, the catalyst concentration is 2 per cent A decrease in this concentration from 2 to 1 8 per cent means a change in surface of 10 per cent, so that when the catalyst is deposited at the surface of the promoter small changes in concentration of promoter produce important alterations in reaction velocity Hurst and Rideal's[1] case of copper promoted by palladium is in this latter category They found an optimum promoter effect at 0 2 per cent palladium At a concentration of 1·7 per cent palladium, the catalytic activity had fallen to that of the unpromoted copper catalyst

The surface conditions in promoted catalysts are obviously complex. A very considerable increase in the number of cases studied is much to be desired Not only should the reactivity of the promoted catalyst be studied, but determinations of adsorptions on the same samples as are used for the activity tests should also be made. The adsorptions should reveal more readily the changes in the surface conditions. Simplification of the problem would be secured by eliminating all support materials in such experiments, since they introduce a new variable into an already complex problem. Hurst and Rideal made one set of adsorption measurements on their promoted copper catalyst, which showed the variation in adsorption previously recorded. It is to be regretted that similar measurements on the whole series of promoted catalysts were not made. If the adsorption measurements were coupled with measurements of heat of adsorption, some data on the problem of activation by promoters might also be secured.

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[1] *J Chem Soc*, 1924, **125**, 685

The really interesting problem which the study of promoter action in its relation to concentration suggests is the reason why such minute amounts of promoter effect such marked changes in activity. Thus, in the case studied by Medsforth a concentration of 0·5 per cent ceria in the nickel catalyst causes a tenfold increase in reaction rate. Assuming uniform distribution of promoter in the catalyst, this represents one molecule of ceria in every 1130 atoms of copper in the catalyst surface This minute change in surface concentration brings about a tenfold increase in catalytic activity. This strongly suggests that, of the atoms in the surface of a catalyst, very few indeed possess marked catalytic activity Armstrong and Hilditch,[1] discussing the small amount of toxic material necessary for total suppression of catalytic activity, conclude that it is probable that an active catalyst is merely an average term expressing a surface on which a number of patches of maximum activity occur, the greater part of the surface being of perhaps a quite low order of activity. This opinion, based upon a study of poisons, is at one with the view put forward here with respect to the mechanism of promoter effect in minute concentrations. In Chapter VI., in the discussion of poisons, the quantitative evidence for this point of view will be detailed.[2]

The mechanism of co-activation.—Conclusions parallel to those just recorded as to the mechanism of promotion in hydrogenation processes have been reached by several workers in respect to the mechanism of co-activation found in the use of mixed oxide catalysts in oxidation processes. Extent of adsorption, the nature of the adsorbed gases, enhanced activity at interfaces, the removal of impurities by the added agent, and the influence of the admixed substance on the rates of several component reactions of the process are all cited in the succeeding paragraphs.

Bray and Almquist[3] attribute the activity of a mixture of two oxides to an increase in the rate of desorption of reaction products,

[1] *Trans. Farad. Soc.*, 1922, **17**, 670

[2] For a detailed discussion of the concept of a composite catalytic surface with isolated centres of high activity see Rideal, *Conseil Solvay*, April 1926; Taylor, *Fourth Report, Committee on Contact Catalysis*, *J. Phys. Chem.*, 1926. Also *Proc. Roy. Soc.*, 1925, **108A**, 105.

[3] *J. Amer. Chem. Soc.*, 1923, **45**, 2305.

or an increase in the rate of reaction within the film, due to what may be considered a partial chemical reaction between the two oxides, a neutralisation of the valence forces of each other

Whitsell and Frazer[1] conclude that manganese dioxide is the initial cause of oxidation at low temperatures in Hopcalite mixtures The oxidation process may be catalytic or occur at the expense of the oxide oxygen The purer the catalyst, that is, the freer from adsorbed potash, the more rapidly was it able to take up oxygen fast enough to make the process catalytic This points to a mechanism of alternate oxidation and reduction Too strong ignition of the preparations, even though alkali-free, gave a dense product resembling natural manganese dioxide and entirely inactive Whitsell and Frazer also incline to the view that the cupric oxide in a mixture may cut down adsorbed alkali or affects the way it is held, so that its poisonous effect is annulled They note that pure manganese dioxide and mixtures of this with copper oxide lose oxygen to the air at room temperatures, and that the activity because of this is greatly increased by the fineness of division of the particles

Benton[2] attacked the problem of co-activation by studying adsorptions of carbon monoxide (and hydrogen) by various oxides and mixtures He concludes that there are two types of adsorption, a primary, specific adsorption, chemical in nature, and a secondary, physical, or pore adsorption By comparison of the adsorptions of oxygen, carbon monoxide, and carbon dioxide he deduces the relative magnitudes of primary adsorption of the monoxide on various oxides and mixtures, and shows that the order of such adsorption is the order of their catalytic activity in oxidation processes He concludes, therefore, that primary adsorption of carbon monoxide is the first stage in the catalytic process, and is followed by desorption of carbon dioxide Benton shows that there is no parallelism between secondary adsorptions and catalytic activity, and that, therefore if total adsorptions measured include both primary and secondary adsorptions such total adsorption may give no clue at all with respect to catalytic activity He concludes that, on silica and charcoal adsorptions are largely physical or secondary, with conspicuous exceptions in the case of charcoal with the gases oxygen and chlorine

Promoter Action and Co-activation in Homogeneous Catalytic Reactions

The outstanding example of promoter action in homogeneous systems is the well-known neutral salt effect in reactions catalysed by the hydrogen ions of strong acids The inversion of cane sugar, the hydrolysis of esters, the dehydration of hydroxy acids to form lactones, keto-enol tautomerism, and other reactions catalytically accelerated by the use of strong acids, all provide this interesting case of promoted catalysis. If, in addition to a strong acid, a neutral salt of that acid is added to the reaction mixture, it is found that the velocity of reaction is increased. As the neutral salt alone has no appreciable catalytic effect, the case is one of simple activation or promoter action rather than of co-activation. It is beyond the scope of this section to detail all the work which has been accomplished or the varied views which have been put forward to explain this phenomenon. They will be separately treated in subsequent sections of the book. It is desirable, however, to point out here that the many attempts which have been made to account for the phenomena all have this in common, that they attempt to account for the observed acceleration by assumptions, for which experimental evidence is also sought, as to the concentration of either the catalyst on the reacting species or both. And the belief is common to all the investigators concerned that, when these several factors shall have been successfully stated, the observed acceleration will be found to be consonant with the ordinary laws of reaction kinetics. This attitude of mind might well be adopted by workers in all branches of the study, not only of promoter action but also of catalysis generally.

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[1] *J. Amer Chem Soc*, 1923, **45**, 2848

[2] *J Amer Chem Soc*, 1923, **45**, 887, 900

Price[1] studied very thoroughly the interaction of potassium persulphate and potassium iodide,

$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2,$$

and the influence of catalysts on the same. He found that ferrous sulphate was a good catalyst, copper sulphate less efficient. Both these catalysts accelerated reaction in proportion to their concentrations in the reaction mixture, but the effect of the two salts together was more than additive. The accelerations observed always exceeded those calculated on the assumption that the individual activities were additive. Manganese and zinc sulphates, which are themselves only slightly active, gave additive results when mixed with copper sulphate. With ferrous sulphate, on the contrary, the observed acceleration was less than the calculated result. Price was unable to give a reason for the catalysis observed or for the co-activation.

The oxidation of hydriodic acid by hydrogen peroxide in presence of iron and copper salts was studied quantitatively by Brode.[2] He showed that ferrous sulphate was a very good catalyst, copper sulphate a poor accelerant. When together, however, one mol of copper sulphate in 100,000 litres was readily manifest. This joint action of the two salts had previously been employed by Traube[3] in testing for hydrogen peroxide in the presence of acids by means of starch-potassium iodide. The iron-copper salt mixture is active in concentrated acid solutions, whereas in such solutions iron salts alone are inactive. Neither iron nor copper sulphates increased the catalytic activity of molybdic or tungstic acid when used as an additional catalyst in the reaction. Molybdic and tungstic acids also behaved additively when used together

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[1] *Zeitsch. physikal Chem.*, 1893, **27**, 474.

[2] *Zeitsch. physikal. Chem.*, 1901, **37**, 257.

[3] *Ber.*, 1884, **17**, 1062.

Bohnson and Robertson[1] have made a very thorough study of the mechanism of this activation of iron salts by copper salts in the decomposition of acid solutions of hydrogen peroxide They find that for a given concentration of iron salt, either sulphate or chloride, there is a maximum rate of reaction with about one millimol of added copper salt per litre This maximum effective concentration of copper appears to be independent of the concentration of iron salt The extent of promotion (measured by the promotion factor which is the ratio of the maximum rate to the normal rate for iron alone) is independent of the acid concentration and temperature The extent of promotion is much greater for ferric sulphate than for ferric chloride, although the maximum rate obtained in each case is the same The promotion factors for the two systems approach each other as the concentration of iron approaches zero

As to the mechanism of the promoter action Bohnson and Robertson conclude that the facts are best explained thus (*a*) the iron salt is the primary catalyst by virtue of its ability to form an intermediate compound, probably H_2FeO_4, (*b*) the copper salt is a secondary catalyst accelerating both the formation and subsequent decomposition of the intermediate product The effect of the secondary catalyst is dependent upon its concentration only for very small quantities, a maximum effective concentration being noted The mechanism of the secondary catalysis has not been explained That the suggested secondary action is real is deduced from the following experiment Two equal portions of a solution of barium ferrate in acetic acid were allowed to react with equal quantities of hydrogen peroxide To one of the samples a very little copper acetate was added The oxygen was evolved much more rapidly in this than in the one to which no copper salt was added. It may be observed that the effect is peculiar to copper compounds, since nickel, cadmium, mercury, barium, lead cobalt, zinc, tin, and magnesium salts appear to retard the reaction in presence of iron salts In sulphate systems, silver appears to have a slight accelerating effect This singular behaviour of copper is probably significant in the solution of the problem of the secondary catalysis.

Bredig and Brown[2] have found that in the catalytic oxidation of aniline by sulphuric acid, according to the equation

$$(C_6H_5NH_2)_2SO_4 + 28H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 28SO_2 + 12CO_2 + 3H_2O,$$

copper sulphate and mercurous sulphates are together more active than their separate catalytic activities would suggest Bredig and

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[1] *J Amer. Chem. Soc*, 1923, **45**, 2512

[2] *Zeitsch physikal Chem*, 1903, **46**, 502.

Brown consider that a reciprocal oxidation and reduction of copper and mercury may be the cause of the unusual results. Only one series of data is given in the research. Hence, it is not possible to say whether either one of the two is particularly susceptible to activation or what relation holds between the acceleration noted and the proportion of salts present. Further work is needed to elucidate these points. The mechanism suggested by the above equation seems also to be impossibly complex, although Bredig and Brown say that the equation quantitatively represents the course of events in very dilute aniline solutions.

SUPPORTED CATALYSTS

The form of the catalyst.—In contact catalysis, the form of the catalytic agent is of considerable importance. The striking feature common to most of the contact catalysts is their porous or finely divided structure Indeed, this structure may be regarded as characterising the successful contact agent. In several cases the preliminary phase of activation of a catalyst is accompanied by a change from a massive form to a finely divided structure. Thus, the platinum gauze catalysts used in the oxidation of ammonia by air or oxygen at high temperatures change from a smooth, plane-surfaced wire to a corrugated material. Similar changes in physical form are shown by silver gauze [1] when used for the catalysis of hydrogen-oxygen mixtures. The catalytic activity of copper wire can be greatly enhanced by submitting it to alternate oxidation and reduction of the oxide at successively lower temperatures. In this way copper catalysts can be secured which will promote oxidation of carbon monoxide, admixed with air or oxygen, at a temperature of 100° C. The copper wire suffers, in the process, a physical change similar to that with platinum and silver. These several methods of activation are, in reality, the production of supported catalysts. The wire core acts as a support material for the active, finely divided material produced on the surface by the process of activation. The mechanism of the activation [2] is to be ascribed partially to the increase in surface area of catalyst; that is, the adsorption per unit mass of catalyst is increased with a resultant increase in reaction per unit mass in unit time. The activation, however, also results undoubtedly in a change of the nature of the adsorption per unit surface of area. The evidence previously cited, and confirmed in a later section in the discussion of poisons, that a catalyst surface is in reality a surface on which a number of patches of maximum activity occur, the greater part of the surface being of low activity, when applied to this problem of activation of massive wire catalysts indicates that in the activation process the number of positions of maximum activity is markedly increased. The disordered arrangement of metallic atoms produced in the activation process is more favourable to the existence of such active patches than is the normal crystal-lattice arrangement of the atoms in a smooth-stranded wire. Langmuir believes that the activation process may also operate favourably to catalysis by changing the normal spacing of the atoms to one more favourable for the adsorption of the reacting gas molecules in such configurations as are conducive to interaction. These several points of view with respect to the mechanism of activation have only received the beginnings of experimental verification. Full experimental confirmation is to be desired.

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[1] Bone and Wheeler.

[2] Bancroft, *First Report, Committee on Contact Catalysis*, 1922; Langmuir, *Trans. Farad. Soc.*, 1922, **17**, 607; Taylor, *J. Franklin Inst.*, 1922, **197**, 1.

In the production of active catalytic agents the method of conduct of the process frequently yields a supported catalyst without general recognition of the fact. Kelber showed[1] that nickel oxide *per se*, when reduced at about 300° C., gave a moderately active catalyst, but when reduced at 450° C. gave a product of but feeble activity. Nickel oxide deposited upon kieselguhr and reduced at 450° C. gave a catalyst much more active than the metal catalyst prepared at 300° C. These conclusions were confirmed by Armstrong and Hilditch,[2] who showed that a reduction at higher temperatures gives rise to considerable shrinkage in the volume of the metal catalyst. This shrinkage and loss of catalytic activity is largely suppressed if the active material is spread upon an inert support. These facts are apparent from the data of the following table.

Source of Material	Nickel Oxide			Reduced Nickel		
	Density	Apparent Volume in c.c.	Temperature Reduction	Density	Apparent Volume in c.c.	Catalytic Activity
Powdered fused oxide	6·96	0·35	500° C.	8·14	0·52	None
Precipitated hydroxide	5·41	0·87	300° C.	7·85	0·83	Fair
Do.	5·41	0·87	500° C.	8·18	0·56	Very little
Oxide on kieselguhr	1·63	3·22	500° C.	1·85	2·67	Very active

In discussing these results, Armstrong and Hilditch remark that "it has frequently been observed, with unsupported nickel oxide, that partially reduced oxide is more active than the same when completely reduced. Since, as our bulk gravity figures show, there is a tendency to contraction when a light, precipitated oxide is reduced, it is obvious that a partially reduced oxide will consist of a film of nickel dispersed over the central core of each particle, and it is practically certain that the superior activity of this product over the fully reduced metal is due to its being a 'supported' catalyst (nickel distributed on nickel oxide) and therefore of the same type, although not of the same degree of activity, as nickel upon a support such as kieselguhr."

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[1] *Ber.*, 1916, 49, 55, 1868.

[2] *Proc. Roy. Soc.*, 1921, 99A, 490.

The superiority of the catalyst spread upon kieselguhr is to be attributed to the nature and extent of distribution of the metal and to the fact that the support does not shrink upon heating, its bulk determining, almost wholly, the bulk of the final product. The support acts as an anchor to the metal deposited upon it and inhibits the sintering or crystallisation which occurs with the unsupported catalyst. The occurrence of sintering with the unsupported catalyst is readily seen from the data in the previous table at 300° C. and 500° C. for the reduction of the hydroxide, the apparent volumes at the two temperatures being 0·83 and 0·56 respectively. This sintering occurs with most unsupported catalysts not only at high reduction temperatures but also when catalysts prepared by reduction at low temperatures are subjected to successively higher temperatures. The sintering is roughly characterised by the change in apparent volume. The change of adsorptive capacity of the sample is, however, a much more sensitive criterion of the occurrence of sintering.[1] The extent to which this occurs may be illustrated by the following figures[2] on unsupported copper and nickel before and after a heat treatment following a reduction:

Catalyst	Heat Treatment	Adsorption of Hydrogen at 0° C. and 760 mm.
A. 100 gm. active Cu	No heat beyond reduction of oxide at 200° C.	3·70 c.c.
B. ..	A. Heated to 450° C. for 1·5 hours	1·15 ,,
C. 27 gm. active Ni	Obtained by reduction of oxide at 300° C.	35 ,,
D. ..	C. Heated at 400° C. for 4 hours	16 ,,

Adsorptive capacity is also a good index of the extent of distribution of the metal catalyst on a suitable support material, and also of the non-sensitivity of such a supported catalyst to heat treatment. Gauger and Taylor[3] readily obtained adsorptions amounting to 5 c.c. per gram of nickel at 0° C. and 760 mm. with this catalyst spread on diatomite brick. The most highly adsorptive sample of unsupported nickel prepared in the same manner showed an adsorption of 1·3 c.c. hydrogen per gram of nickel under the same circumstances. There is reason to believe that this sample was in reality a supported catalyst, namely, a partially reduced sample, nickel on a nickel oxide support. Furthermore, in contrast to the data on unsupported nickel catalysts cited in the previous table, nickel catalysts on diatomite brick could be prepared by reduction at 500° C, or could be subjected to heat treatment at such temperatures, without loss of adsorptive capacity Pollard[1] found that adsorption measurements could not be duplicated satisfactorily with platinum black, as the gases could not be pumped off completely without heating to 300° C, at which temperature the platinum sinters to such an extent that the adsorption changes very much Platinised asbestos, however, can be heated to 400° C without undergoing any change

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[1] Taylor, 3rd Report on Cont. Cat., *J. Phys. Chem.*, 1924.

[2] Pease, *J. Amer. Chem. Soc.*, 1923, **45**, 1196, 2235. Beebe and Taylor, *J. Amer. Chem. Soc.*, 1924, **43**, 43.

[3] *J. Amer. Chem. Soc.*, 1923, **45**, 920.

The increased catalytic activity per unit mass of catalytic agent employed, secured by spreading the catalyst on a support, means economy of material in the catalytic operation It is for this purpose that the more expensive contact agents were thus first supported, the use of platinised asbestos and platinised magnesium sulphate being good examples At the same time, other desirable properties in the catalyst may be secured If a catalyst material be too fine, considerable resistance is offered to the passage of reacting gases, and this frequently results in channelling through the contact mass, with a corresponding decrease in efficiency The incorporation of the catalytic mass upon a suitable support may obviate such difficulties In exothermic catalytic reactions there is the danger that overheating, and consequent destruction of the activity, of a catalyst mass may occur Quite recently in such cases use has been made of the metal aluminium as catalyst support material, thermal equilibrium in the catalyst system being thereby facilitated[2] The metal support is employed in a granular form, obtained by allowing the molten metal to cool slowly in trays, the mass meanwhile being vigorously shaken

Support materials and poisons. - Rosenmund and Langer[3] have shown that the nature of the support material is of importance in protecting the catalyst against poisons as well as in influencing the catalytic activity With palladium catalysts on various supports the influence of arsenious oxide and carbon monoxide as poisons was studied, in the reduction of cinnamic acid Kieselguhr-palladium catalysts showed the least activity and greatest sensitivity to poisons Blood charcoal gave the most active and most resistant preparations In these two cases activity and resistance run parallel Barium sulphate supports are more active than pumice, the latter are more active in presence of the poisons The effect of the supports is evidently a function of the adsorptive capacity of the support for the poison It acts in these cases as a purification agent in the catalyst system

Adsorption of reactants by support materials. -- It is possible that one of the functions of the support material is to provide the catalyst with a reservoir of one or more of the reactants Thus, R A Beebe[4] has shown that asbestos, suitable for use as a support for platinum in the production of contact mass for sulphur dioxide oxidation, adsorbs 0·79, 0·10, and 0·04 c.c. of nitrogen and 53·0, 11·3, and 2·0 c.c. of sulphur dioxide per gram at 0°, 110°, and 218° C. respectively. Similarly, magnesium sulphate was shown to adsorb marked quantities of the same gases. Diatomite brick, which forms a good support material for the cuprous chloride used in the oxidation of hydrogen chloride by the Deacon chlorine process, can be shown to adsorb large amounts of hydrogen chloride. Russell[1] has shown that pumice used as a support for nickel adsorbs 1·2 c.c. of nitrogen per gram at 110° C., and still larger quantities of carbon dioxide. The question as to whether this adsorption by the support of one of the reactant gases facilitates the progress of the catalytic reaction has still to be decided. More must be learned concerning the mechanism and characterisation of activation of reacting species In the meantime the existence of such adsorptive capacities by the support materials must be remembered when measurements of adsorption by contact materials spread upon supports are being made.

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[1] *J Phys Chem*, 1923, **27**, 356

[2] Barrett Co, Edgewater, N J, Stockholm's Superfosfat Aktiebolaget, S P, 1921.

[3] *Ber*, 1923, **56**, 2262

[4] Thesis, Princeton University, 1924, *J Phys Chem*, 1925, **29**, 1325.

Nature of support materials.—A variety of substances have been employed as support materials. In addition to those already alluded to, mention may be made of glass, wool and silica fibres, fibrox, various porous siliceous materials such as fireclay, alundum, and unglazed porcelain, the various forms of charcoal, anhydrous salts and porous oxides obtained by calcination of suitable materials or by dehydration of gelations, precipitates or gels.

Gels as support materials. Considerable attention has been devoted recently to the use of gels as support materials for catalytic agents, and some striking results have been indicated. An impetus was given to this work by the development of the technical production of silica gel adsorbents by Patrick[2] and of base-exchanging silica gel and alumina-gels by Wheaton and J. Crosfields.[3] Patrick has patented[4] the use of impregnated silica gels as catalytic agents, having mentioned specifically the production of platinised silica gels for sulphur dioxide oxidation. He has shown also that silica gels impregnated with iron oxide show marked efficiency in the oxidation of sulphur dioxide. As an example of the preparation of such a gel, Patrick cites the production of an iron oxide gel. One hundred c.c. of a 5 per cent ferric chloride solution is mixed with 200 c.c. of sodium silicate containing 1 per cent Na_2O. After the mixture has set, the gel may be broken up and washed free from chlorides without loss of iron. The impregnated ferric oxide may be reduced to iron by the action of hydrogen. In place of the silicate, an aluminate, stannate, titanate, tungstate, or zirconate may be used. The products cited in the patent include silica with iron, copper, or

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[1] Thesis, Princeton University, 1924, *J. Phys. Chem.*, 1925, **29**, 1325.

[2] B.P. 136543/1919; U.S.P. 1297724/1919.

[3] B.P. 177746/1922.

[4] B.P. 159508/1921.

nickel, silica and iron oxide with copper, magnesium, cadmium, zinc, and manganese oxides, and silica and alumina with copper oxide.

Reyerson and Patrick[1] have studied metal-impregnated silica gels obtained by reducing metals from solutions of their salts by means of hydrogen adsorbed in silica gel at -20° C. The metals form a black deposit on the gel, and in the case of palladium, platinum, and copper marked reaction between hydrogen and ethylene has been obtained at room temperatures.

Choice of support materials. The choice of material to be employed is generally determined by processes of experimentation. As with the choice of catalysts generally, no sure guiding principles can be laid down. Experience shows, however, that in a great many cases use of a given catalyst support brings about a serious diminution in catalytic efficiency, generally attributed to a functioning of the support as a negative catalyst. Obviously, with a catalyst which is poisoned, for example, with sulphur, the presence of sulphur in the catalyst support is not permissible. The extraordinary sensitivity of certain catalysts to minute impurities restricts severely the number of possible supports. In reactions which are conducted at high temperatures, also, the possibility of interaction between catalyst and support material must be constantly envisaged. Especially in the case of oxide catalysts is this necessary, owing to the ease of combination with siliceous materials with formation of non-active silicates. In such cases, catalyst supports which are basic in character are to be favoured. The ideal support, therefore, should be a porous material free from impurities negatively catalytic to the contact body, incapable of interaction with the catalyst, and, if possible, itself positively catalytic, even though feebly so, to the reaction in which it is to be employed.

PROTECTED CATALYSTS

Colloidal catalysts when employed in catalytic reactions oftentimes lose their activity by agglomeration of the colloidal particles. The decrement in surface thereby resulting is reflected in a decrease in catalytic activity. Such colloidal catalysts may be stabilised by the addition of various agents, and the use of such "protected" colloidal catalysts is now standard practice. Paal and his co-workers[2] made use of a water-soluble protective colloid, the sodium salts of protalbinic or lysalbinic acids, to stabilise colloidal platinum and palladium. Skita,[3] who has detailed in a comprehensive manner the literature of the subject, employed an acid stable protective colloid such as gum arabic. Gelatine and glue have also been employed.

[1] *Colloid Symposium Monograph*, p. 119, Madison Wis., 1923.

[2] *Ber.*, 1905, **38**, 1398, 1406, 2414; 1907, **40**, 1392, 2201, 2209; 1908, **41**, 805, 2273, 2282; 1909, **42**, 1544, 1553, 2239, 3930; 1913, **46**, 1297.

[3] *Ber.*, 1911, **44**, 2862; 1912, **45**, 1627.

The function of the added agent is to protect the colloid particles from agglomeration in the reaction media in which they are placed. This is brought about by the presence of the protecting agent on the outside of the particles of colloidal catalyst. The stabilisation thereby secured is obtained, however, at the expense of the catalytic activity. This was shown by Gröh [1] in the stabilisation of colloidal platinum by gelatine. Even small quantities of the gelatine exert a most marked retarding influence on the rate at which hydrogen peroxide is decomposed by the platinum, as the following table shows.

Per cent Gelatine	Time for Half Decomposition	Per cent Gelatine	Time for Half Decomposition
0·000	100	0·05	620
0·001	437	0·10	983
0·01	460	..	..

The gelatine, however, increases the stability of the colloidal metal solution, and tends to prolong its period of activity by preventing its precipitation by electrolytes.

Rideal [2] studied the protective action of gum arabic on colloidal platinum or palladium in the catalytic hydrogenation of phenyl propiolic acid. It was found that gum arabic in small amounts increased and then in larger amounts decreased the rate of the reduction process when the sols were prepared in the presence of the protective agent. The increase is to be attributed to an increased dispersion of the colloidal metal brought about by the presence of the protecting agent. In studying mixed platinum and palladium sols, Rideal found that "in all cases where the sol was prepared from platinum containing small quantities of palladium there was a very marked improvement in stability and resistance to age over those prepared from the pure salts. This suggests the hypothesis that promoters may function in part as peptising agents for colloidal catalysts or for catalysts which pass through a colloidal stage at some point in their preparation." Bancroft points out [3] that in addition to the possibility of increased dispersion, it is also possible that the reaction may take place more rapidly at the interface between the two metals.

Iredale studied [4] the parallelism between the effect of protective colloids on the catalytic decomposition of hydrogen peroxide and their efficiency as protective colloids. He found that the stronger a substance is as a protective colloid the greater its inhibitory power on catalytic activity. The order of inhibitive effect is gelatine and

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[1] *Zeitsch. physikal Chem.*, 1914, **88**, 414; Bancroft, Second Report, *J. Phys. Chem.*, 1923, **27**, 892.

[2] *J. Amer. Chem. Soc.*, 1920, **42**, 749.

[3] Second Report, *J. Phys. Chem.*, 1923, **27**, 894.

[4] *J. Chem. Soc.*, 1921, **119**, 109; 1922, **121**, 1536.

glue > egg albumin > gum arabic > sucrose, the last appearing not to affect the reaction at all With gelatine the inhibitory effect was noticeable with one part of the protective colloid in twenty million parts of water By determining the smallest amounts of different protective colloids which perceptibly retard the catalytic decomposition of hydrogen peroxide, Iredale obtained inhibition numbers which he then compared with the gold numbers, using gelatine as standard. The inhibition numbers for gelatine, egg albumin, dextrine, and starch were found to be 100, 20, and 0·33, while the gold numbers were correspondingly 100, 20, 0·66, and 0·40 Iredale therefore concluded that the inhibition number may be defined as the percentage of protective colloid, which is just insufficient to inhibit catalytic action The ratios of these numbers for different protective colloids are of the same order of magnitude as the ratios of the gold numbers

Rocosolano[1] found a similar relationship between the inhibitory action of gelatine and gum arabic With sodium lysalbate the rate of decomposition of hydrogen peroxide in presence of colloidal platinum decreases to a minimum with increasing concentration of protective colloid, but passes through a minimum and then increases This latter effect is to be attributed to the alkalinity of the protective colloid, which overcomes the inhibitory effect

Bancroft[2] concludes that the essential difference between the "supported" and the "protected" catalyst is that in the former the platinum is on the outside of the asbestos, whereas the gelatine is on the outside of the platinum in the latter

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[1] *Compt rend*, 1921, **173**, 44, 234

[2] *Colloidal Behaviour*, p 274 (McGraw-Hill, 1924)

CHAPTER VI

CATALYST POISONS AND THE INHIBITION OF HOMOGENEOUS CHEMICAL REACTIONS

THE phenomenon of "poisoning" is limited to contact catalytic reactions. The term "poisoning" was originally given to the reduction in activity of contact catalytic agents which is brought about by the presence of substances foreign to the reaction under study and present in relatively small amounts. The use of the term has been extended, and it is now recognised that poisoning to various degrees may occur, requiring relatively small or large amounts of a foreign substance, and, also, that even the reacting species or the resulting products may "poison" the reaction at the catalyst surface, slowing down the rate at which the process takes place.

The attention of the scientist to the phenomenon dates almost from the earliest studies of catalysis, as has been indicated in the historical introduction Dobereiner's platinum "sickened" with use. Faraday investigated "some very extraordinary interferences" with the catalytic combination of hydrogen and oxygen in contact with platinum. Turner and Henry gave much attention to the phenomenon, and out of their researches developed methods of preferential catalytic combustion. The parallelism existing between the inhibition of contact catalysts and of enzymes probably led to the extended use of the term "poisoning" for the phenomenon.

The occurrence of poisoning in technical catalytic processes has been a determining factor in the industrial application of catalysis. The transfer of a catalytic process, perfectly practicable on the laboratory scale with purified materials, to the stage of technical production, in which materials of the same degree of purity are less easily obtained, is very frequently the central problem, determining ultimate success or failure. The early patent to Phillips on the oxidation of sulphur dioxide in presence of platinum only attained commercial exploitation when the problem of the removal of arsenical and other poisons from the sulphur gases was attained. All earlier commercial efforts to secure the catalytic production of sulphur trioxide failed, owing to poisons in the reacting gases. Volatile silicon compounds lead to the poisoning of platinum in the ammonia oxidation process. Traces of sulphur compounds present in the reacting gases are poisonous in the ammonia synthesis reaction and in hydrogenation processes, with the normal catalysts for these operations. Oxides of sulphur and arsenic impair the activity of cuprous chloride catalysts in the Deacon chlorine process.

Classification.—Poisons may be either permanent or transitory. Thus the silicon compounds present in the ammonia-air mixture and in the oxidation of ammonia in contact with platinum gauze are oxidised to silica, which is deposited in part on the gauze and destroys its activity by covering up the platinum surface. The poisoning is permanent. Dust may also be included in the category of permanent poisons. Hydrogen sulphide and sulphur compounds transform an iron catalyst in ammonia synthesis and a nickel catalyst in hydrogenation processes to the corresponding sulphides, whose catalytic activity is negligible. The effect of the sulphur is cumulative and non-reversible, and it is necessary to regenerate a catalyst so poisoned by suitable means. In the case of an iron catalyst poisoned by sulphur, it is necessary to oxidise the sulphide completely to the oxide and then regenerate the metal by reduction. All cases of permanent poisoning require such a renewal of the contact mass before original activity is regained.

Transitory poisons are those which are only effective so long as they are present in the reacting system. After the removal of the harmful constituent from the reactants, provided the action has not been too prolonged, the original activity of the catalyst is restored. Faraday found that the inhibitory action of carbon monoxide on the platinum catalysis of hydrogen and oxygen only lasted so long as carbon monoxide is present in the reacting gases. Water vapour is a transitory poison in ammonia synthesis in presence of an iron catalyst, at a reaction temperature of 500° C. Low conversion efficiencies are obtained when the drying of the nitrogen-hydrogen mixture is incomplete. But the original activity is restored when thoroughly dried gases are turned into the reaction system.

It should be noted that the classification is dependent both on the catalyst and the reaction. A poison may be both transitory or permanent according to the catalyst used. In the case of ammonia synthesis, using uranium carbide (which changes to nitride with use) as catalyst, water vapour, oxygen, and carbon monoxide are permanent poisons. They convert the nitride to an irreducible uranium oxide, catalytically inert. It is this factor that has militated against the technical use of the otherwise very excellent uranium compound as a catalyst in ammonia synthesis. As already mentioned, water vapour is a transitory poison in ammonia synthesis with an iron catalyst. Furthermore, it is probable also that water vapour is the real poison in the case of oxygen and carbon monoxide poisoning in ammonia synthesis in presence of iron, since both these gases undergo quantitative transformation to water vapour and to methane and water vapour respectively under the conditions of the synthetic process.

The mechanism of poisoning.—It is now generally agreed that the inhibition of reaction produced by poisons is to be ascribed always to the diminution of the active catalyst surface by the poison. The reduction in surface may be mechanical and permanent, as in the illustrations of permanent poisoning already given. The reduction may also be temporary, and in this case it is brought about by preferential adsorption of the poison on the catalyst surface. Experimental data to illustrate this explanation of temporary poisoning have long been available, but it is only recently that the full realisation of their significance has been attained. Bancroft [1] has been especially instrumental in securing this recognition. His correlation of the literature has been supplemented by experimental data designed to give this point of view a quantitative basis.

Faraday's observation [2] that "the very power which causes the combination of oxygen and hydrogen is competent under the usual casual exposure of platina, to condense extraneous matters upon its surface, which, soiling it, take away for the time its power of combining oxygen and hydrogen, by preventing their contact with it", was extended by Henry.[3] He recognised that the presence of the reaction product might slow up the rate of reaction. He proved this by showing that the reaction rate between carbon monoxide and oxygen in contact with platinum was accelerated if the carbon dioxide produced was continuously removed from the reaction system by adsorption with caustic potash. Schönbein [4] pointed out that the hydrides of sulphur, selenium, tellurium, phosphorus, arsenic, and antimony were all active in retarding the reaction between air and hydrogen or ether in the presence of platinum. He was of the opinion that the inhibition was due to the formation of a film over the platinum, probably solid, not that of a gas film. This is not a necessary conclusion, as we now know that preferential adsorption may be strong, even of gases in minute concentrations, and an adsorbed gas film is just as effective in covering an active catalyst surface as a solid film. Maxted has shown,[5] however, that platinum or palladium may decompose hydrogen sulphide, the sulphur remaining on the surface, so that Schonbein's reasoning may be correct in certain cases.

Bredig's studies [6] of the analogy between colloidal metals and enzymes showed that the activity of colloidal platinum in the decomposition of hydrogen peroxide could be inhibited by minute amounts of foreign substances just as the function of enzymes in the same reaction could be similarly suppressed Bancroft has compiled the following table relative to the effect of minute concentrations of substances as poisons in the decomposition of hydrogen peroxide by means of platinum and by hæmase, the active enzyme of the red blood corpuscles In the second and third columns of the table are given the molar concentrations at which the poisons reduce the rate of decomposition to *approximately one-half of the* rate in absence of the poison.

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[1] *J. Physical Chem.*, 1917, **21**, 767; *First and Second Reports, Committee on Contact Catalysis*, 1922, 1923.

[2] *Experimental Researches*, 353.

[3] *Phil. Mag.*, 1836 [3], **9**, 324.

[4] *J. pr. Chem.*, 1843, **29**, 238.

[5] *J. Chem. Soc.*, 1919, **115**, 1050.

[6] *Zeitsch. physikal. Chem.*, 1899, **31**, 258; 1901, **37**, 1, 323; *Ber.*, 1904, **37**, 798; *Zeitsch. Elektrochem.*, 1908, **14**, 51.

Poison	*Colloidal Platinum*	*Hæmase*
H_2S	M/300,000	M/1,000,000
HCN	M/20,000,000	M/1,000,000
$HgCl_2$	M/2,000,000	M/2,000,000
$HgBr_2$		M/300,000
$Hg(CN)_2$	M/200,000	M/300,000
I_2 in KI	M/5,000,000	M/50,000
$NH_2OH . HCl$	M/25,000	M/80,000
$C_6H_5NHNH_2$		M/20,000
$C_6H_5NH_2$	M/5,000	M/400
As_2O_3	M/50	No poisoning at M/2,000
CO	Very poisonous	No poisoning
HCl	M/3,000	M/100,000
NH_4Cl	M/200	M/1,000
NHO_3	No poisoning	M/250,000
H_2SO_4	" "	M/50,000
KNO_3	" "	M/40,000
$KClO_3$	Slight poisoning (?)	M/40,000

There is an undoubted parallelism between the two cases, since adsorption is specific, however, it is easy to understand that the same substances should not necessarily poison both platinum and hæmase, since, also, the extent of adsorption at a given concentration varies with the adsorbent, a given concentration of poison should not necessarily poison them both to the same extent.

The investigations of Meyerhof[1] on the "narcotic" action of alcohols and urethanes in the catalytic decomposition of hydrogen peroxide by platinum may also be cited in reference to the adsorption view Ultramicroscopic evidence showed that the addition of the narcotics did not cause an agglomeration of the colloidal particles, and therefore the decreased rate of decomposition is not attributable to such cause Meyerhof considers it probable that a surface film of the poison is formed over the catalytic agent, which prevents contact of the reacting substances with the catalyst The retardation caused by alcohols and urethanes in the action of invertase on sugar is also attributed by Meyerhof[2] to displacement of the sugar from the surface of the colloidal invertase. Cases of agglomeration of colloidal particles are, however, not unknown, as was pointed out by Bredig.[1]

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[1] *Pflüger's Archiv*, 1914, **157**, 307

[2] *Pflüger's Archiv*, 1914, **157**, 251

The researches of Bodenstein and his co-workers on the kinetics of heterogeneous gas reactions demonstrated conclusively that both the reaction products and one or other of the reactants could act as poisons to the catalyst in the reaction. Fink's work with Bodenstein on the mechanism of sulphur dioxide oxidation[2] in contact with platinum established kinetically, as well as by experimental measurement of adsorption, that the sulphur trioxide produced inhibited the reaction by reason of its strong condensation on the surface of the platinum. This observation was incorporated in the Bodenstein-Fink theory of gas reactions at catalytic surfaces. The reaction velocity was assumed to be determined by the rate of diffusion of the reactant gases through a film of adsorbed resultant, which film was assumed to vary in thickness with the partial pressure of such resultant. Langmuir has shown,[3] however, that the kinetic data may receive a different explanation. If only unimolecular layers of adsorbed gas are possible—and Fink's measurements indicate the essential correctness of this view—the reaction rate is conditioned by the fraction of the surface which is bare of the strongly adsorbed gas under the experimental conditions. The strongly adsorbed gas may be one of the reactants, as the work of Bodenstein and Ohlmer[4] on the combination of carbon monoxide and oxygen in contact with quartz glass indicates. In this case, carbon monoxide is a poison to its own reaction. The experimental data are successfully interpreted by Langmuir in a manner analogous to that obtaining with sulphur trioxide. Bodenstein and Fink assumed that the surface of the glass was covered with an adsorbed layer of carbon monoxide of a thickness proportional to the pressure of the gas. By then assuming that the oxygen has to diffuse through the layer of carbon monoxide before coming into contact with the quartz glass where it reacts with the monoxide, it was possible to explain the fact that the reaction rate was proportional to the oxygen pressure and inversely proportional to the pressure of carbon monoxide. This naturally involves an assumption that the quartz glass is capable of adsorbing the gas in films many molecules deep. Bodenstein and Fink did not measure the adsorption of quartz glass for carbon monoxide. Some unpublished measurements by Benton indicate that the adsorption of this gas on quartz glass ground to almost colloidal dimensions is abnormally small, so small that the Bodenstein-Fink assumption is very improbable indeed. Even Langmuir's assumption that the surface is nearly covered with a layer one molecule deep seems to require some modification, namely, that only those portions of the quartz surface which are catalytically active are nearly covered with carbon monoxide. This would mean that the "elementary spaces" of the surface are not all catalyticall active. Langmuir's method of treatment would then be restricted t the "elementary catalytic spaces" Further evidence for this ide of "elementary catalytic spaces" will be given in a succeeding section when more quantitative evidence will be brought forward

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[1] *Zeitsch. physikal. Chem.*, 1899, **31**, 332.

[2] *Zeitsch. physikal Chem.*, 1907, **60**, 1.

[3] *J. Amer. Chem. Soc.*, 1916, **38**, 2286.

[4] *Zeitsch. physikal. Chem.*, 1905, **53**, 166.

It is of interest to record that Bodenstein and Ohlmer showed that, in contact with crystalline quartz, the reaction between carbon monoxide and oxygen follows the ordinary stoichiometric equation This result really requires further experimental test, as it involves a most interesting phenomenon The carbon monoxide is apparently a poison with the fused quartz glass and not a poison with the crystalline variety of the same molecular species

Adsorption by poisoned catalysts.- A number of isolated observations occur in the older literature concerning the influence of poisons on the adsorption, more generally designated the occlusive power, of catalytic agents Berliner showed [1] that traces of fatty vapours from the air or from the grease on the stopcocks will decrease the occlusion of hydrogen by palladium from about nine hundred volumes to nothing. Mond, Ramsay, and Shields [2] showed that mercury vapour had the same action. Fink [3] demonstrated sulphur trioxide adsorption, but did not determine the adsorption of other constituents in its presence Paal and Steger [4] showed that mercury vapour cuts down the adsorption of palladium hydrosol for hydrogen and decreases the catalytic activity towards oxy-hydrogen gas

The most complete experimental study of adsorption in presence and absence of poisons has been carried out by Maxted,[5] who has demonstrated definitely the parallelism between the action of poisons on adsorption and on catalytic activity The occlusive power of palladium for hydrogen in the presence of occluded hydrogen sulphide was shown to vary linearly with the content of inhibitant The decrease in activity caused by the poisons, lead, mercury, zinc, sulphur, and arsenic, is directly proportional to the concentration of inhibitant from zero concentration in platinum up to that producing practically complete inactivity The presence of lead decreases both the hydrogen adsorption by, and the catalytic activity of palladium The amount of lead, as poison, required to reduce the catalytic activity to one-half, is very much less than that which reduces the occlusive power to one-half its original value. This may be explained by the fact that while occlusion is not confined to the surface, catalysis is mainly a surface phenomenon It will be shown, however, that this observation, repeated with metals which show little or no occlusion such as palladium shows, leads to very interesting conclusions concerning the nature of catalyst surfaces and their reactivity. Maxted also studied the catalysis of hydrogen peroxide decomposition by platinum in solutions containing mercuric chloride, mercuric nitrate, and lead acetate. The curve obtained by plotting the catalytic activity of the platinum against the poison content is approximately linear until at least 70 per cent of the original activity has been suppressed. Preliminary experiments on adsorption indicated that inhibitants such as catalytically poisonous metals, in dilute solutions, are adsorbed strongly by platinum catalysts ; but the adsorption is incomplete, except probably in the presence of relatively large concentrations of catalyst. This result has recently been quantitatively confirmed by Maxted.[1] It is worthy of note that arsenic, in the form of sodium arsenate, has a very low toxicity to platinum, whereas, in the form of arsine, it has a high activity as an inhibitant This distinction was earlier noted by Bredig. It is a result which is entirely explicable on the basis of the newer theories with respect to the electronic configurations of arsine and arsenates.

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[1] *Wied Ann*, 1888, **35**, 903.

[2] *Zeitsch physikal Chem*, 1898, **25**, 667.

[3] *Loc. cit.*

[4] *Ber*, 1918, **51**, 1743.

[5] *J Chem. Soc*, 1919, **115**, 1050, 1920, **117**, 1280, 1501; 1921, **119**, 225, 1280; **1922** **121**, 1760

Langmuir[2] showed that carbon monoxide was adsorbed tenaciously by platinum at room temperatures, and that at a temperature below 450° K. it should be impossible, in any reasonable time, to remove an adsorbed film of carbon monoxide merely by pumping off the gas with a good vacuum pump.[3] Taylor and Burns[4] confirmed this conclusion, working with platinum black, and found that it was necessary to burn the gas off with oxygen and then remove the excess oxygen with hydrogen The hydrogen could then be removed by heating in a vacuum. When platinum black was not subjected to this treatment after having been exposed to carbon monoxide, but was merely evacuated at 110 C., a subsequent measurement of hydrogen adsorption showed three volumes at 25° C., whereas the true value on a clean surface was 6·85 volumes. This is a decrease of approximately 60 per cent. In an analogous way the adsorption of carbon monoxide itself at 110° C. declined from 19·2 volumes on a clean surface to 7·3 volumes when the surface had been exposed previously to carbon monoxide and then only evacuated. This would indicate that it is possible to render only about 40 per cent of the platinum surface free from carbon monoxide by heating the vessel to 110° C. in a vacuum of 0·002 mm. for a moderate period of time. This tenacity with which carbon monoxide is held and the diminished adsorption thereby produced is a convincing demonstration of the cause of inhibition noted by Harbeck and Lunge[5] when carbon monoxide was present in the hydrogenation of ethylene.

Taylor and Burns' catalyst was undoubtedly contaminated with stopcock grease and was not readily susceptible to exact adsorption easurements, since, if heated above 110° C., coalescence of th latinum black occurred. Pollard[1] obtained their results even mor strikingly. *With platinised asbestos kept very clean from grease, he obtained one hundred and sixty volumes of hydrogen adsorbed per volume of platinum. On introducing carbon monoxide, the hydrogen adsorption dropped to about seven volumes, which is practically negligible under the conditions of the experiment.*

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[1] *J. Chem. Soc.*, 1925, **127**, 73.

[2] *J. Amer. Chem. Soc.*, 1918, **40**, 1398.

[3] *Trans. Farad. Soc.*, 1922, **17**, 641.

[4] *J. Amer. Chem. Soc.*, 1921, **43**, 1283.

[5] *Zeitsch. anorg. Chem.*, 1898, **18**, 50.

By studying the influence of poisons on the adsorptive capacity and catalytic activity of copper, Pease[2] avoided Maxted's difficulties with palladium, with which metal both surface phenomena, solution and compound formation with hydrogen may occur. Pease admitted mercury to a copper catalyst on which measurements were made both of adsorption and catalytic activity before and after poisoning. About 20 c.c. of mercury vapour (measured at 0° C. and 760 mm.) were admitted to the copper, which was then heated to 200° C. for one half-hour and evacuated. After cooling, the mercury had disappeared and the catalyst was unchanged in appearance. The adsorptions at 380 mm. pressure of hydrogen and ethylene, respectively, were found to be 3·25 c.c. and 8·55 c.c. before poisoning and 0·15 c.c. and 6·70 c.c. after poisoning. The rate of reaction was reduced to about one-half per cent of its value before poisoning. This reduction in rate is achieved with a reduction of hydrogen adsorption to about one-twentieth of its former value. The ethylene adsorption was only moderately diminished. This experimental evidence is conclusive in one respect. It indicates that the reactivity is not exactly proportional to the extent of the adsorbed gas. In other words, not all the adsorbed gas is rendered catalytically active in the process of adsorption.

Pease's subsequent work[3] has abundantly confirmed these conclusions and amplified them. Carbon monoxide, which is strongly adsorbed by copper, is a marked poison for the reaction between ethylene and hydrogen. By successively reducing the quantities of carbon monoxide introduced into the reaction system, Pease has shown that the carbon monoxide molecules required to render the reaction negligible under the conditions of the experiment are markedly less than the number of hydrogen molecules capable of being adsorbed by the copper catalyst. This seems to be quantitative evidence that only a fraction of the surface which is capable of adsorbing the hydrogen is capable of activating it sufficiently to promote reaction. It is apparently quantitative confirmation of a suggestion of Armstrong and Hilditch[4] and Rideal,[5] that an active catalyst is merely an average term expressing a surface on which a number of patches of maximum activity occur, the greater part of the surface being of quite a low order of activity.

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[1] *J. Physical Chem.*, 1923, **27**, 370.

[2] *J. Amer. Chem. Soc.*, 1923, **45**, 1196, 2235.

[3] *Amer. Chem. Soc.*, Spring Meeting, 1924. Pease and Stewart, *J. Amer. Chem. Soc.*, 1925, **47**, 1235.

[4] *Trans. Farad. Soc.*, 1922, **17**, 670.

[5] *J. Chem. Soc.*, 1922, **121**, 314.

The experiments of Maxted[1] on the poisoning of colloidal palladium for the hydrogenation of oleic acid had two similar conclusions. The falling off in catalytic activity on the addition of lead is found to be in direct proportion to the amount of lead adsorbed, over a wide range corresponding with the poisoning of the patches of maximum activity. Hydrogenation proceeds at a much slower rate on the less active portions to which the lead may be caused to adhere, but less strongly than on the active patches, thus necessitating a larger concentration of lead salt in solution. More detailed study of these cases is needed, and examples should be multiplied. It would be desirable to have not only data on adsorptions of the gases at various partial pressures, but also adsorptions of the gases from mixtures.

The work of Pease further indicates that from the study of poisons more may be learned with respect to the mechanism of activation and of adsorption. The work with mercury poisoning of the copper catalyst showed that the poisoning effect was most marked on the hydrogen and negligibly so on the ethylene. This indicates that reaction velocity is primarily dependent on the activation of the hydrogen As the physical characteristics of the gas would suggest also, the slight influence of mercury poisoning on the ethylene adsorption tends to show that the adsorbed ethylene is largely present in condensed films, not in surface-unimolecular gas film complexes

Progressive poisoning. If a catalyst surface is composed of patches of varying activity it is evident that progressive poisoning of the surface ought to be attainable. With small amounts of a suitable poison the more highly activating centres of the surface will be rendered inactive. A reaction requiring high catalytic activity would cease after such poisoning, but one not requiring so active a catalyst might proceed. This phenomenon seems to have been realised in several cases.

One such case has been studied by Vavon and Husson[2] with the deliberate object of establishing the existence of progressive poisoning. The poisoning studied was that of platinum black by carbon disulphide. The authors showed that 5 grams of acetophenone in alcohol containing 0·2 gram of platinum fixed 25 c.c. of hydrogen on the average in six minutes. After the addition of 0·4 mg. of carbon disulphide no adsorption of hydrogen occurred. If, however, 1 gram of cyclohexene was then added to the solution, hydrogen was again taken up, 25 c.c. being fixed on the average in 4 minutes. In a second example a three-stage process of progressive poisoning was obtained. Five grms. of propyl ketone in 50 c.c. of glacial acetic acid containing 3 grms. of platinum showed a hydrogen adsorption of 25 c.c. in 4 minutes. The addition of 2·3 mg. of carbon disulphide stopped the adsorption. If 2 grms. of piperonal were now added to the solution, hydrogen absorption again commenced at a rate of 25 c c in 3·5 minutes. The further addition of 1·4 mg of carbon disulphide again caused the hydrogen absorption to cease The catalyst was still capable of some hydrogenation, for when 2 grms. of nitrobenzene were added to the solution the absorption of hydrogen again commenced, 25 c c *being taken up on the average in 1·75 minutes From this it may be concluded that nitrobenzene is readily reduced with practically inert catalysts* Propyl ketone needs an active catalyst.

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[1] *J. Chem. Soc.*, 1920, 117, 1801; 1921, 119, 1280.

[2] *Compt. rend.*, 1922, 175, 277.

This behaviour is very reminiscent of the observations of Sabatier[1] with reference to hydrogenation of the benzene nucleus with nickel Sabatier showed that it required an active nickel catalyst, prepared by reduction at low temperatures, to effect the hydrogenation of the benzene nucleus. On the other hand, less active catalysts, prepared at higher reduction temperatures, while incapable of effecting the hydrogenation of the benzene nucleus, were nevertheless quite useful and efficient in the hydrogenation of the single ethylenic bond The work of Gauger and Taylor,[2] already cited, showed that the higher temperature of reduction resulted in a catalyst of lower adsorptive capacity for hydrogen than one obtained by low temperature reduction The effect of heat treatment of a catalyst is, therefore, quite analogous to the effect of poisoning Pease confirmed this with experiments both on the reaction velocity of hydrogenation and the adsorptive capacity of copper for the gases hydrogen and ethylene Pease writes "In the course of the experiments on the catalytic combination of ethylene and hydrogen, the effect on both catalytic activity and adsorptive capacity of partially deactivating a copper catalyst by heating it to 450° in a vacuum was determined The effect of deactivating this sample of copper by heating was in a general way similar to the effect of deactivating the sample by poisoning it with mercury. The curves have been moved over toward the pressure axis to nearly parallel positions, at the higher pressures at least The heating has, however, decreased the hydrogen adsorption relatively less than the poisoning and the ethylene adsorption relatively more Thus, at one atmosphere, the decrease in hydrogen adsorption amounts to 70 per cent, while the decrease in ethylene adsorption amounts to 22 per cent These are to be compared with decrease of 92 per cent for hydrogen and 14 per cent for ethylene, caused by mercury poisoning The absolute decreases at one atmosphere are 2 60 for hydrogen and 1·95 for ethylene It will be seen that these figures are much more nearly of the same order than in the case of copper poisoned with mercury

"The decrease in catalytic activity in the ethylene-hydrogen combination accompanying these decreases in adsorption amounted to 85 per cent. Just as in the case of the poisoning by mercury, one must go to very low pressures to find a corresponding decrease in adsorption, indicating that it is the strong (low pressure) adsorption which is mainly responsible for catalytic activity."

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[1] *Catalysis in Organic Chemistry*, Sabatier, translated by Reid (Van Nostrand, 1923).

[2] *J Amer Chem Soc*, 1923, **45**, 920.

Beneficial poisoning.—Since partial poisoning may be secured, it is evidently possible that use may be made of it to achieve certain reactions whilst obviating others. A very obvious application is in the case where a catalytic process proceeds too far with an active catalyst. By minimising the activity of such a catalyst or poisoning the more highly reactive patches with the requisite poison, the reaction may be stopped at the desired stage. Many investigations into the conditions necessary to secure a good yield of a desired product may, in reality, be unconscious applications of this procedure of beneficial poisoning. An example suggestive of this may be quoted

Armstrong and Hilditch[1] have shown that in the catalytic dehydrogenation of ethyl alcohol in the presence of copper, the presence of water in the alcohol improves the yield of acetaldehyde relative to that of hydrogen. Thus, at 300° C., whereas anhydrous alcohol only gave an aldehyde-hydrogen ratio of 67 per cent, alcohol containing 8 per cent water gave a 95 per cent ratio. With the anhydrous alcohol, there is a marked increase in the yield of gaseous products, principally methane, carbon monoxide, and carbon dioxide in addition to the hydrogen. It is evident that, with the anhydrous alcohol, secondary decomposition of aldehyde is much more pronounced than with alcohol containing water. Thus, methane and carbon monoxide result from one such secondary decomposition :

$$CH_3CHO \longrightarrow CH_4 + CO.$$

Evidently the water acts as a beneficial poison in that it poisons the catalyst for such secondary decompositions, which apparently require a larger energy of activation, in all probability as a result of strong preferential adsorption on the catalyst surface. Armstrong and Hilditch showed, by passing aldehyde vapour together with water over a copper catalyst, that the water had a considerable protective influence on the aldehyde.

The dehydrogenation of alcohol in the presence of nickel occurs at lower temperatures than in the presence of copper, but the secondary decomposition is very high. The data of Armstrong and Hilditch show that dehydrogenation occurred at 250° C. The aldehyde-hydrogen ratio was only 35·7 per cent and the evolved gas contained 60 per cent hydrogen, 20 per cent carbon monoxide, and 15-17 per cent methane. Evidently, in this case, the 8 per cent of water in the alcohol used was not sufficient to protect the aldehyde produced. It would be interesting to extend this study of dehydrogenation with nickel in the presence of water to see whether the secondary decomposition could be largely suppressed by increase of water content in the alcohol, since the low yields obtained with copper at the higher temperatures could b partially restored by such an increase in water content

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[1] *Proc. Roy. Soc.*, 1920, **97A**, 262.

Palmer's study[1] of this same reaction *in the presence of a coppe catalyst indicates that alcohol itself plays the same rôle as the water in the experiments already cited* He showed that, below 300° C, the secondary products were negligible when the dehydration of alcohol occurs; but, if a mixture of acetaldehyde and hydrogen is passed over the copper catalyst between 250° and 300° C, much of the aldehyde is decomposed Bancroft has suggested[2] that such cases might be called "protective poisoning"

The same procedure was used during the years 1917 1919 for the production of ethylene from alcohol in presence of kaolin Instead of a low temperature process, the reaction was conducted at red heat and the products were protected from decomposition by using alcohol-water mixtures, even though the process was dehydration

The researches of Rosenmund, Zetsche, and Heise[3] have shown that partial poisoning may be used to attain new organic preparations and to manipulate a given reaction to yield various desired end products Thus, if benzoyl chloride is dissolved in pure benzene and then reduced by hydrogen in presence of colloidal palladium, practically no benzaldehyde is produced If, instead of pure benzene, ordinary benzene be used, a good yield of benzaldehyde is obtained This indicates the presence in ordinary benzene of a substance or substances which poisons the reduction of benzaldehyde to benzyl alcohol That the poisoning is due to the sulphur compounds in ordinary benzene seems probable from the fact that additions of sulphurised organic compounds to pure benzene produced like effects Quinoline, quinoline heated with sulphur giving an impure thioquinanthrene, purified thioquinanthrene, xanthone, and dimethylaniline were all employed as beneficial poisons Thus, the addition of 1 mg of thioquinanthrene to a system containing 2 grms of benzoyl chloride and 0 7 grm of palladium in 10 c c of xylene, gave a yield of 78 per cent of benzaldehyde when reduction was carried out at 150° C Impure thioquinanthrene under the same circumstances gave a 90 per cent yield If, instead of the sulphurised quinoline, 0·1 grm of distilled quinoline was added to the xylene, practically no benzaldehyde was obtained, reduction to the benzyl alcohol stage occurring The addition of xanthone to the reaction mixture promotes reaction between unchanged benzoyl chloride and benzyl alcohol with the formation of benzyl benzoate. This ester is the principal product when toluene is used as solvent in place of xylene. In toluene, reduction of benzyl benzoate by hydrogen to toluene and benzoic acid does not readily occur, whereas, in xylene, this further reduction occurs freely Thus, with palladium partially poisoned in a variety of ways, the reduction of benzoyl chloride by hydrogen may be directed to yield, in the main, one or other of the substances benzaldehyde, benzyl alcohol, benzyl benzoate, dibenzyl ether, or toluene, the product obtained being determined by the nature and amount of the added substance.

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[1] *Proc Roy Soc*, 1920, **98**A, 13

[2] *First Report, Committee on Contact Catalysis*

[3] *Ber*, 1921, **54**, 425, 638, 1092, 2033, 2038

Zetsche has extended the work to the catalytic dehydrogenation of alcohols, with accompanying oxidation of the hydrogen produced, by passage of air through the solution. With copper as a catalyst, the yield of benzaldehyde from benzyl alcohol dissolved in cymene is increased when quinoline is added to the solution. Addition of nitrobenzene still further increases the yield. There is a possibility that in this case there is a coupled catalytic reaction, dehydrogenation of the alcohol and reduction of the nitro-compound. Nickel and silver as catalysts are also more efficient when quinoline is present, but, with these metals, benzyl ether and resins are produced. Much more detailed study of these cases is needed before a complete understanding of the particular mechanisms can be attained.

The vapour phase dehydrogenation of methyl alcohol to yield formaldehyde is probably also an additional case in which beneficial poisoning may occur. As is well known there is a considerable tendency for the formaldehyde produced to undergo secondary decomposition to carbon monoxide and hydrogen. Low yields are frequent in the technical operation Steam may in this case be used as a protective poison

Rate of adsorption and poisoning.—In catalytic gas reactions the normal time of contact of the flowing gases with the catalytic material is of short duration. Thus, in the case of ammonia oxidation with a platinum gauze catalyst, the time of contact is of the order of a hundredth of a second. With such brief periods of contact it is evident that any decrease in the rate of adsorption will have a corresponding effect on the velocity of reaction.[1] It is well known that the attainment of equilibrium in adsorption from a mixture of gases is markedly longer than from a single gas. It is evident, therefore, that the effect of catalyst poisons may be due in part to a reduction in the velocity with which adsorption of the reacting substances occurs. No experimental data on this point are available, but certain figures in connection with charcoal adsorptions give the idea some support. Harned[2] has shown that the rate of adsorption of chloropicrin by a charcoal the surface of which has been cleaned by washing with chloropicrin, is much greater in the initial stages of adsorption than is the case with a charcoal which has not been so cleaned, although the final equilibrium is apparently about the same in the two cases. Patrick and his co-workers[3] have shown that the hysteresis shown in the adsorption curves of gases on silica gel is to be attributed to the influence of gaseous impurities on the velocity of adsorption of the gases bein studied

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[1] Taylor, *Trans. Amer. Electrochem. Soc.*, 1919, **36**, 149.

[2] *J. Amer. Chem. Soc.*, 1920, **42**, 372.

[3] *J. Amer. Chem. Soc.*, 1920, **42**, 946; *J. Physical Chem.*, 1925, **29**, 601.

Poisoning and poison concentration.—The data of Maxted, alread cited (p. 133), show a linear proportionality over a considerable rang for gaseous poisons adsorbed on the catalysts from gases containin small amounts of gaseous poison These results are readily understandable, since, for very low gas pressures, the adsorption of a gas i essentially proportional to the gas pressure

In those cases in which the poison concentration attains much higher values such simple relations will not hold. Thus, in the experiments of Bodenstein and Fink, the velocity of sulphur trioxide formation from sulphur dioxide and oxygen varies inversely as the square root of the sulphur trioxide concentration In the reaction of carbon monoxide-air mixtures at quartz surfaces the reaction velocity s inversely proportional to the carbon monoxide concentration Langmuir has shown [1] that special considerations as to the spaces occupied on the surface by the several gases may be adduced to ndicate the observed reaction mechanism In general, the reaction mechanism is determined by the distribution of the reactants and poisons between the gas phase and the surface layer of the contact mass. This distribution will be by no means constant as to the distribution of the poison with wide variations in the reactant concentrations Hence, a varying reaction kinetics for one and the same reaction at different stages of the process in presence of a poison can be anticipated The data of Bodenstein and his co-workers on the kinetics of heterogeneous reactions give abundant illustrations of this fact. The distribution between the gas phase and the surface may also be influenced by the nature of the surface, its concentration of active patches This leads to the intriguing possibility that, by suitable preparation of the catalyst surface, the deleterious effect of poisons may be minimised, a result which would have considerable technical importance

Poisoning and temperature.—Since temporary poisoning is generally due to adsorption on the surface of the catalyst, and since adsorption is, in general, an exothermic process, it is evident that, with rise in temperature, the fraction of the surface which is covered with poison at any given partial pressure of the poison will decrease The catalytic efficiency of the surface will therefore increase at a greater rate than is the case if no poisoning is present For, in addition to the normal increase in reaction velocity with temperature, there will be the increase due to increase in available surface The temperature coefficient of a catalytic reaction poisoned by a temporary poison will, therefore, be larger than that of the normal catalytic reaction This point has been indicated by W C. McC. Lewis [2] It holds true whether the resultants of the reaction or a body foreign to the reaction is the poisoning constituent, provided the poisoning is attributable to a reversible adsorption. If one of the reactants is responsible for the poisoning effect, the variation of reaction velocity with temperature will depend on the extent to which the surface is covered with the reactant poison. With the active surface almost completely covered with this poison a high temperature coefficient will result. As the temperature rises and the surface covered by poison becomes less and less, the conditions will change towards a state in which the adsorbed poison behaves more and more as an ordinary constituent of the reaction process—it ceases to be a poison.

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[1] *J. Amer. Chem. Soc*, 1916, **38**, 2263

[2] *J Chem. Soc.* 1919 115 182

There are few quantitative measurements which can be cited in support of these observations; there are, however, numerous qualitative observations which substantiate the conclusions. Thus, the inhibitory influence of water vapour, oxygen, and carbon monoxide on the synthesis of ammonia from its elements in contact with iron catalysts becomes progressively less important as the temperature rises. Dougherty and Taylor[1] showed that the poisoning effect of carbon monoxide on the vapour phase hydrogenation of benzene in presence of nickel was pronounced at 100° C., but became less effective as the temperature was raised.

Permanent poisons, since they completely destroy the catalytic activity of the surface they cover, do not produce any abnormality in the temperature coefficient. Their effect is to decrease the extent of surface, to a degree independent of the temperature of operation of the catalyst.

Poisoning and apparent equilibria.—Bancroft has pointed out[2] that, in the case of a reaction poisoned by one of the products, the apparent equilibrium attained will depend on the quantity of catalytic agent employed. If there is a large excess of catalytic agent, the reaction will run to an end or true equilibrium before the catalyst is entirely poisoned. If, on the other hand, there is only a small amount of catalytic agent it will very soon be poisoned and we shall have an apparent equilibrium reached from only one side, which will vary with the amount of catalyst used. As an example of such a case, Bancroft cites the work of Neilson[3] on the splitting of salicin and amygdalin by platinum black. In the former case the salicylic acid produced, and, in the latter case, the hydrocyanic acid produced, are toxic to the platinum. If means were taken to ensure removal of the hydrocyanic acid formed, Neilson found that the splitting of the amygdalin proceeded further than in the absence of such precautions.

This effect of poisons on equilibrium should be quite marked with enzyme catalysts. In such cases there is the possibility that not only adsorption of poisons may occur but also agglomeration of the enzymes as a result of the action of reaction products. Apparent equilibria will result dependent on the amount of enzyme used. This has already been observed.[1]

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[1] *J. Physical Chem.*, 1923, **27**, 548.

[2] *First Report, Committee on Contact Catalysis*, 1922.

[3] *Amer. J. Physiol.*, 1906, **15**, 148.

THE INHIBITION OF HOMOGENEOUS CHEMICAL REACTIONS

Catalysis is concerned, in the main, with the acceleration of reactions occurring with diminution of free energy. The catalyst may be distributed molecularly in a homogeneous reaction system or it may be an interface in a heterogeneous system. In the latter case, the catalytic efficiency of the surfaces may, as we have shown, be diminished by the effect of poisons concentrated thereon. In homogeneous systems, where the catalyst is molecularly dispersed, a retardation suffered by the reaction system is not usually regarded as a case of poisoning, though the effect produced may, as we shall see, involve a mechanism very similar to that involved in the poisoning of an active centre in a heterogeneously distributed catalyst. It has been usual to characterise such cases of retardation in homogeneous reactions by the term "negative catalysis." For several reasons the term is not very suitable and it seems preferable to group the many phenomena included in the study under the more inclusive title, inhibition of homogeneous chemical reactions.

Catalytic reactions occur when the change from an initial set of reactants to a final set of resultants occurs more readily in presence of the catalyst than in its absence. In homogeneous systems it has been shown that this necessarily involves some association between reactants (A) and catalyst (C), whereby the products (B) result more readily from the associated complex or compound (A C) than from the reactants (A) alone. The case strictly parallel to this involving retardation, implies an association between A and C such that the product B is less readily produced. If the association assumed involved a very considerable diminution in the active mass of A, it is evident that a retardation would result. It is evident, however, that this is by no means the only way in which retardation of reaction may occur. If the reaction A to B be catalysed by the presence of a powerful catalyst X, then the addition of anything which will decrease the concentration of X in the reacting system will effect a retardation of the observed reaction process. It has been shown also in the discussion of the energy of activation of chemical processes (Chapter III.) that the possibility exists of the energy produced by chemical reaction being transferred in some manner or other to reactant molecules, thereby activating them and causing a sequence or chain of reactions. Any substance, added to a reaction system in which such a chain mechanism is possible, and causing the length of the chains which occur to be shortened, will effect a retardation of the reaction velocity. It is with a variety of retarded chemical processes, involving one or other mechanism such as those just outlined, that the present section on the inhibition of homogeneous chemical reactions will deal.

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[1] Tammann, *Zeitsch. physikal. Chem.*, 1895, **18**, 426; Kastle and Loevenhart, *Amer. Chem. J.*, 1900, **24**, 491; Bancroft, *J. Physical Chem.*, 1918, **22**, 39.

Historical.—Though less assiduously studied, examples of inhibition have been recognised almost as long as examples of catalytic acceleration. Thènard,[1] in his investigations of hydrogen peroxide, found both catalysts and inhibitors for the decomposition of this substance. He showed that the peroxide was stable in acids, but underwent rapid thermal decomposition in presence of alkalis. The inhibitory power of oxygen on the photochemical combination of hydrogen and chlorine was early ascertained and received quantitative study in the classical researches of Bunsen and Roscoe.[2] It will be shown that this is one of many such inhibitions of photochemical processes, including the inhibition of the photochemical decomposition of hydrogen peroxide. The study of reaction kinetics in the early days of the development of physical chemistry provided numerous examples of inhibition susceptible to quantitative study. The influence, on the hydrolytic activity of weak acids, of neutral salts having a common anion was a very striking example of the inhibition of a catalysed reaction. The researches of Muller[3] on the inhibitory power of hydrobromic acid in the hydrolytic decomposition of bromo-succinic acid provided a good example of auto-inhibition or auto-retardation. The researches of Bigelow[4] on the inhibitory power of such substances as mannite, benzaldehyde, and benzyl alcohol on the rate of oxidation of sodium sulphite solutions by dissolved oxygen initiated quantitative investigations of the inhibitory power displayed in a wide variety of autoxidation processes. It is in the prevention of autoxidation and in the preservation of hydrogen peroxide that the principal technical applications of inhibition have been made. Water has been shown to function as inhibitor in a number of reactions occurring in non-aqueous solvents. Bredig and Lichty[5] investigated the retarded decomposition of oxalic acid in concentrated sulphuric acid solutions when minute amounts of water are added. Water similarly inhibits the conversion of acetophenoxime to acetanilide in sulphuric acid solutions,[6] and also the decomposition of triethyl sulphine bromide[7] in acetone and acetic acid solutions. The most important example, however, of the inhibitory power of water is in its action on the esterification of organic acids in alcoholic solutions, as investigated by Goldschmidt and his co-workers[8] and by

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[1] *Ann. Chim. Phys.*, 1818, **9**, 314.

[2] *Pogg. Ann.*, 1855, 96 ; 1857, 100 ; 1857, 101 ; 1859, 108.

[3] *Zeitsch physikal. Chem.*, 1902, **41**, 483.

[4] *Zeitsch. physikal. Chem.*, 1893, **12**, 329.

[5] *Zeitsch. Elektrochem.*, 1906, **12**, 450 ; *J. Physical Chem.*, 1907, **11**, 256.

[6] Lobry de Bruyn and Sluiter, *Proc. Akad. Wetenschap Amst.*, 1904, **6**, 773.

[7] *V.* Halban, *Zeitsch. physikal. Chem.*, 1909, **67**, 129.

[8] *Ber.*, 1895, **28**, 3218 , 1906, **39**, 711 ; *Zeitsch. Elektrochem.*, 1906, **12**, 432.

Lapworth and his students.[1] In the decomposition of diazo-esters in alcohol,[2] water is also an inhibitor

Classification.—It is difficult, in the absence of any well-defined body of scientific opinion as to the precise mechanism of inhibitory action, to adopt a completely satisfactory classification of inhibited reactions. Tentatively, however, it seems desirable to base a system of classification on the several mechanisms which have already been offered in explanation of the phenomena, and to discuss the more important individual examples of each type in some detail The inhibited reactions may be discussed under the following headings

(*a*) Reactions inhibited by reduction of the concentration of a positive catalyst

(*b*) Reactions inhibited by reduction of the concentration of a reacting constituent

(*c*) Reactions inhibited by diminution of a chain of reactions in which activating energy is produced

It will not be possible in every case to assign a given inhibition with certainty to one or other of these classes Other classes of inhibition may also be required Experimental work is needed before such can be accomplished

Reactions inhibited by reduction of the concentration of a positive catalyst.—This class was formerly the most important class of inhibited reactions It was definitely established by the work of Titoff[3] on the rate of oxidation of sodium sulphite solutions by dissolved oxygen. Bigelow[4] and Young[5] had shown that a bewildering variety of chemical agents diminished the rate of oxidation of such substances Titoff was able to show that the presence of extremely minute amounts of foreign substances, for example 10^{-13} molar copper sulphate, was sufficient to produce a perceptible acceleration of the rate of oxidation of such solutions Luther is credited by Titoff with the conclusion, from a quantitative study made by the latter, that the function of the inhibitor was to suppress these powerful positive catalysts and so retard reaction Titoff found that the rate of reaction was inversely proportional to the concentration of inhibitor, I He attributed this to the formation with the catalyst, C, of an inert complex, IC, whence, by the law of mass action, for the process.

$$\mathrm{I}+\mathrm{C} \rightleftarrows \mathrm{IC},$$

$$[\mathrm{C}]=K\frac{[\mathrm{IC}]}{[\mathrm{I}]}.$$

The square brackets denote concentrations, and K is the mass action constant. If the measured rate of reaction be proportional to [C] it will also be proportional to $\frac{[IC]}{[I]}$, and, therefore, inversely as [I] so long as [C] is small compared with [I], or, alternatively, so long as the concentration of complex [IC] is relatively large, for then [IC] can be regarded as constant.

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[1] *J Chem Soc*, 1908, **93**, 2167, 2187

[2] Bredig and Frankel, *Zeitsch physikal Chem*, 1907, **60**, 202

[3] *Zeitsch physikal. Chem*, 1903, **45**, 641

[4] *Zeitsch physikal Chem*, 1898, **26**, 493

[5] *J. Amer Chem Soc*, 1901, **23**, 110, 450; 1902, **24**, 297.

Titoff found in the enormous sensitivity of reactions to minute amounts of accelerating catalysts a ready explanation for the extremely small amounts of inhibitors which were found, in the studies of Bigelow, Young, and Titoff, to be adequate for the inhibition of reaction. Titoff's explanation became, consequently, the most quoted explanation of inhibition. While it is undoubtedly true that such a mechanism will yield the observed inhibitory reaction, it is also certain that Titoff's explanation may not be the only reason for inhibitory action even in the particular case of sodium sulphite oxidation; nor is it the only explanation for the minute amounts of inhibitor required. It will be shown in other sections that further possibilities exist. Such possibilities might even be forecast from the variety of inhibitors found for the reaction. On Titoff's view, one would be compelled to assume a very varied series of complexes between the active catalyst, say the copper ion, and the inhibitors studied.

The inhibitory power of water in the esterification of acids in alcoholic solutions and in the decomposition of diazo-esters in alcoholic solutions, as well as the well-known action of neutral salts of weak organic acids on the hydrolysis of esters in aqueous solutions in presence of the corresponding weak organic acids, probably all represent complex cases of the Titoff type of inhibition. In these reactions the hydrogen ion, in one or other form, either non-hydrated (Lapworth) or alcoholated (Goldschmidt), is a positive catalyst for the reaction. The changes in ionisation and in the extent of hydration or solvation due to the addition of the inhibitor are the complex factors in these cases. They are dealt with in detail in appropriate sections of this book.[1]

The inhibitory power of water on the decomposition of oxalic acid in concentrated sulphuric acid solutions [2] and on the conversion of acetophenoxime to acetanilide [3] in the same solvent, may also be attributed to the removal of a positive catalyst, in this case sulphur trioxide, from the solution by interaction with the added water. The former of these two cases has been particularly well examined from the standpoint of reaction kinetics. This mechanism of inhibition is in agreement with the observation that when 0·05 per cent of water is added at 25° C. the time required to secure the decomposition of oxalic acid increases to over sixfold of that required when no water has been added, and that when the amount of water reaches 0·1 per cent the time is increased nineteenfold. It is also in agreement with the influence of temperature on the inhibitory power, this decreasing as the temperature rises, and is also in agreement with the abnormal temperature coefficient of the reaction, 4·42 at 25° C and 3·35 in the interval 70°-80° C This high coefficient is to be attributed to the joint operation of two factors, the increase of the concentration of SO_3 catalyst with increase of temperature and the ordinary increase in efficiency of the catalyst with temperature Bredig and Lichty showed that alkali sulphates also retard the decomposition Since these form double compounds with sulphuric acid they would also tend to suppress sulphur trioxide in the acid solution

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[1] See p. 160 *et seq.*

[2] Bredig and Lichty, *Zeitsch. Elektrochem.*, 1906, **12**, 450; *J. Physical Chem.*, 1907, **11**, 255.

[3] Lobry de Bruyn and Sluiter, *Proc. Akad. Wetenschap Amst.*, 1907, **6**, 773.

All[1] of these facts are in agreement with the assumption that the inhibition is attributable to compound formation between activated molecules of sulphuric acid and the water molecules as an alternative reaction to compound formation between the active sulphuric acid molecules and oxalic acid, which may be regarded as the preliminary stage in the oxalic acid decomposition The alkali sulphate would behave similarly Making use of compound formation as a criterion of inhibitory power, Taylor found[2] that acetic acid and dimethyl pyrone both behaved as inhibitors of oxalic acid decomposition If this mechanism were the correct one, the inhibitions would fall among those in which the reactant rather than the catalyst was removed by the inhibitor That the function of the water might be the removal of catalytic sulphur trioxide appears more probable to Christiansen,[3] who points out that it is supported by the observation that decomposition of oxalic acid is very rapid in sulphuric acid to which sulphur trioxide has been added

A recent research by Whitford[4] on the decomposition of malic acid in sulphuric acid solutions, and a comparison of the results obtained with the earlier work of Lichty on oxalic acid and the researches of Schierz[5] on formic acid, lends some support to Taylor's theory Sodium, potassium, and silver sulphates, water, dimethyl pyrone, and acetic acid are all found to exert an inhibitory action in the order which the mechanism of compound formation would forecast, that is to say, it is greatest with the sulphates and least with acetic acid. Sulphur trioxide in small concentrations has no effect, in large concentrations it inhibits the reaction, both results contrary to what one would expect on Christiansen's view that the activity of sulphuric acid is to be attributed to its sulphur trioxide concentration. The relative effect of water on the rate of decomposition of oxalic, malic, and formic acids in sulphuric acid is also in agreement with the theory, being most marked with the strongest acid, oxalic acid, and least with formic acid Furthermore, as with oxalic acid, the temperature of the reaction rate is abnormally large, the average value being 3·72 for a ten-degree interval from 20° to 50°.

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[1] *J. Physical Chem.*, 1923, **27**, 322.

[2] Unpublished experiments

[3] *J. Physical Chem*, 1924, **28**, 145.

[4] *J Amer. Chem Soc*, 1925, **47**, 953.

[5] *J Amer Chem Soc.*, 1923, **45**, 447.

Reactions inhibited by reduction of the concentration of a reacting constituent.—It is quite possible to formulate a series of general cases in which inhibitions by reduction of the concentration of a reactant shall occur. Thus, for example, in any reaction in which one of the actual reactants in the process is the ion of an electrolyte, the undissociated electrolyte being either non-reactive or of a lower order of activity than the ion, inhibition will occur whenever any substance is added to the reaction system which represses the dissociation of the electrolyte whose ion is reactive. Conversely, in any reaction in which the undissociated electrolyte is more reactive than its ions, inhibition will occur when, to the reaction system, substances are added which will increase the dissociation of the electrolyte. If in a reaction of either type just discussed the inhibitor results from the reaction, the system will show auto-inhibition or auto-retardation. Examples of these several types are well known and have been comprehensively studied with respect to reaction kinetics.

Muller [1] studied the inhibitory action of hydrobromic acid on the hydrolysis of bromo-succinic acid. Since the hydrogen bromide results from the hydrolytic process, this represents an example of auto-inhibition. Müller showed that the equation

$$dx/dt = k\frac{a-x}{x}$$

more nearly represented the effect of the concentration, x, of the inhibitor, on the rate of reaction, than does an equation formulated by Ostwald for an auto-inhibited process:

$$dx/dt = k_1(a-x) - k_2x(a-x).$$

That this expression of Ostwald cannot be generally applicable is evident from the observation that, with certain values for k_1 and k_2, the value of dx/dt would change sign; that is, the reaction become zero, or would even reverse itself—which has never been observed.

Senter and Porter,[2] dealing with the influence of the hydrogen halides on the hydrolysis of the several halogen acids of acetic, propionic, and butyric acids, with the inhibitory action of nitric acid on the reaction between bromo-substituted aliphatic acids and silver nitrate in alcoholic solutions, and with the problem of inhibition in general, showed that the term involving the inhibitor concentration normally appeared in the denominator. They showed that, in the reactions of the halogen-substituted acids with water, both the undissociated molecule and the anion of the acid undergo hydrolysis at rates definite and distinct for each acid and each ion. Retardation is produced by the halogen acid formed, in those cases in which the rate of hydrolysis of the ion is faster than that of the undissociated molecule This is the case, for example, with bromo-propionic anion and acid The inhibition is, therefore, due to the function of the strong hydrogen halide in altering the relative ratios of the more active anion and the less active molecule of the weak acid They developed the mathematical equations expressing this explanation and showed that the concentration of inhibitor appeared in the denominator of the equations, in agreement with their experimental observations

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[1] *Zeitsch. physikal. Chem.*, 1902, **41**, 483.

[2] *J. Chem. Soc.*, 1911, **99**, 1049.

The inhibitory power of water on the velocity of decomposition of triethyl sulphine bromide in acetone and to a less degree in acetic acid solutions, may be explained on the assumption that the addition of water increases the dissociation of the bromide in the solvent. If the undissociated molecule alone undergoes decomposition, then the mechanism of the inhibitory power is manifest This assumption should be tested Furthermore, it should be noted that this reaction also shows a high temperature coefficient of 3 per 10° rise in temperature with a water concentration as high as 6·7 per cent The reaction also shows an exponential increase in the effect of the concentration of water on the reaction velocity. These observations must be accounted for in a completely satisfactory explanation of this inhibition

A well-known case of inhibition, namely the inhibitory power of hydrogen bromide and of iodine, on the thermal and the photochemical combination of hydrogen and bromine, first studied in detail by Bodenstein and Lind,[1] has recently been elucidated It furnishes a further example of a reaction inhibited by diminution of the concentration of one of the reacting species Bodenstein and Lind showed by a study of the kinetics of the thermal combination that the rate of formation of hydrogen bromide could be represented by an equation of the form

$$\frac{d[2\mathrm{HBr}]}{dt}=\frac{k[\mathrm{H_2}]\sqrt{[\mathrm{Br_2}]}}{m+\dfrac{[2\mathrm{HBr}]}{[\mathrm{Br_2}]}},$$

where the square brackets indicate concentrations of the several reacting species The form of the equation clearly shows the inhibitory influence of the hydrogen bromide formed The explanation of this singular equation was suggested, approximately simultaneously, by Christiansen,[2] Polanyi,[3] and Herzfeld[4] These three investigators assumed that the initial action was a dissociation of bromine into atoms:

$$\mathrm{Br_2}=2\mathrm{Br}. \quad . \quad . \quad . \qquad (\mathrm{I.})$$

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[1] *Zeitsch. physikal. Chem*, 1906, **57**, 168.

[2] *Dansk Vid. Math Phys Medd*, 1919, **1**, 14.

[3] *Zeitsch Elektrochem.*, 1920, **26**, 50

[4] *Zeitsch Elektrochem*, 1919, **25**, 301, *Ann. Physik*, 1919 (4), **59**, 635

By collision of such a bromine atom with a hydrogen molecule, reaction occurred occasionally thus:

$$H_2 + Br = HBr + H. \quad . \quad . \quad . \quad . \quad . \quad (ii.)$$

The resulting hydrogen atoms could disappear in two ways:

$$H + Br_2 = HBr + Br \quad . \quad . \quad . \quad . \quad . \quad (iii.)$$

and

$$H + HBr = H_2 + Br. \quad . \quad . \quad . \quad (iv.)$$

Finally, the bromine atoms, which would otherwise accumulate and produce an ever increasing reaction velocity, must maintain themselves in a stationary state by reason of the reverse reaction to (i.)

$$2Br = Br_2.$$

Such a sequence of reactions gives a kinetic equation of the form obtained by Bodenstein and Lind. On this basis, the inhibitory power of the hydrogen bromide is to be attributed to its capacity to remove hydrogen atoms from the reaction system, these hydrogen atoms being producers of hydrogen bromide by reaction (iii). The inhibitory power of iodine is similarly explained as due to the reaction

$$H + I_2 = HI + I,$$

the iodine atoms being too inert to bring about reactions similar to those between bromine atoms and hydrogen.

This theory of the mechanism of the inhibitory action of hydrogen bromide and iodine, together with the observation of light sensitivity of the hydrogen-bromine reaction at higher temperatures, has led Bodenstein and his co-workers[1] to renewed study of the reaction process. The interesting conclusion from this work is that bromine atoms are by no means so reactive as has been postulated in recent theories of reaction mechanism. Bodenstein and Lütkemeyer[2] conclude that only 1·25 per thousand of the collisions between bromine atoms result in the formation of bromine molecules.

Reactions involving a chain mechanism and showing inhibition phenomena.—*The hydrogen-chlorine combination.*—The photochemical combination of hydrogen and chlorine is the best known example of this class of phenomena. As has long been known, the photo-reaction of the two gases is enormously sensitive to traces of impurities. In this respect ammonia and nitrogenous organic bodies are especially powerful inhibitors of reaction. Special precautions to remove such impurities are necessary if a sensitive reaction mixture is to be obtained.[3] Oxygen, however, forms a very efficient inhibitor of the reaction, and its influence has been studied kinetically by several workers since the original classical investigations of Bunsen and Roscoe[1] It has been shown that the rate of the hydrogen-chlorine combination is approximately inversely proportional to the amount of oxygen present in the reaction mixture

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[1] *Zeitsch. Elektrochem.*, 1924, **30**, 416; *Zeitsch. physikal. Chem.*, 1924, **114**, 208.

[2] *Zeitsch. physikal. Chem.*, 1924, **114**, 208.

[3] See Chapman and Burgess; Chapman and MacMahon, *J. Chem. Soc.*, 1906, **89**, 1402; 1909, **97**, 845; or, for a concise summary, *Treatise on Physical Chemistry*, chap. xviii. pp. 1218-1228 (Macmillan & Co., 1924).

By comparing the light energy absorbed by the system with the chemical energy produced as a result of the light absorption, Bodenstein showed,[2] in 1913, that there was an enormous divergence between the two quantities in a sensitive gas mixture Thus, Bodenstein calculated that, in his most sensitive mixture, for every quantum ($h\nu$) of light energy absorbed, as many as 10^6 molecules of chlorine were caused to react This large divergence from expectations based upon Einstein's Law of the Photochemical Equivalent,[3] according to which there should be equivalence, in pure photo-reactions, between light energy absorbed and chemical energy produced, led to a number of theories[4] to account for the excessive amount of reaction produced by the light Of these, the most popular has been that of Nernst, which, although far from being completely satisfactory as an explanation of all the facts of the photochemical combination of hydrogen and chlorine,[5] nevertheless illustrates well the idea of a chain of reactions and has led to a more detailed study of reactions, which deviate widely from the Einstein Law of the Photochemical Equivalent Nernst assumed that the initial absorption of light resulted in a dissociation of a chlorine molecule into atoms·

$$Cl_2 + h\nu = 2Cl$$

These chlorine atoms were then able to enter a series or chain of reactions, each reaction occurring with free energy decrease and therefore spontaneous, whereby, in each, hydrogen chloride and either hydrogen or chlorine atoms were produced

$$Cl + H_2 = HCl + H,$$
$$H + Cl_2 = HCl + Cl$$

Such reactions continued until the hydrogen and chlorine atoms were lost either by recombination with each other or in some other manner.

It is easy to show that such a mechanism cannot have general applicability. It breaks down, for example, when we come to consider various other halogenation processes in which a similar disparity exists between light energy absorbed and chemical energy produced. It would be difficult to devise analogous chain systems to the above for the reactions between carbon monoxide and chlorine, methane and chlorine, xylene and bromine, in all of which, however, marked deviations from the law of the photochemical equivalent occur and which also show great sensitivity to the presence of inhibitors. The existence of such deviations from photo-equivalence demands, however, some mechanism of reaction whereby initial photo-process is succeeded by a very large number of spontaneous processes, the activating energy for which must come from the reaction energy produced in the processes set in motion by the original photo-reaction. The nature of the energy transfer involved and the steps by which it is achieved are, at the moment, quite unexplained. The problem involved forms a most important phase of our study of the mechanism of chemical change. It is more important and more complex by reason of the fact that such a succession of reactions can be disturbed or diminished by the presence of small quantities of inhibitors. In the succeeding paragraphs examples will be multiplied of reactions which involve some type of chain mechanism and show also the phenomenon of inhibition.

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[1] See, for example, *J Chem Soc*, 1909, **97**, 845, 1919, **115**, 1264, 1923, **123**, 3062, *Zeitsch physikal Chem*, 1913, **85**, 297

[2] *Zeitsch physikal Chem*, 1913, **85**, 351.

[3] *Ann Physik*, 1912, **37**, 832, *Verh Deut Physikal Ges*, 1916, **18**, 315.

[4] *Zeitsch. Elektrochem*, 1916, **22**, 58, 1918, **24**, 335, *Zeitsch physikal Chem*, 1913, **85**, 351, 1923, **106**, 426; *Ber*, 1923, **56**, 696

[5] See *Treatise on Physical Chemistry*, chap xviii p 1226 (D van Nostrand Co., New York, 1924, Macmillan & Co, London, 1925).

In the case of the hydrogen-chlorine combination it is known that the nitrogen-containing organic inhibitors are consumed in the course of the reaction. Their effect, therefore, progressively decreases as the reaction proceeds, and it is to the presence of such bodies that the well-known phenomenon of the induction period in photo-halogenations is to be ascribed.[1] As regards the function of oxygen in the inhibition of the hydrogen-chlorine combination, Weigert[2] and more recently Rideal and Norrish[3] have shown that chlorine sensitises the reaction between hydrogen and oxygen to visible light, and that oxygen is removed from the reaction mixture as water vapour. The reaction velocity is proportional to both the chlorine and the oxygen concentration, so that it seems that the excited chlorine molecule transfers its energy by collision to an oxygen molecule, rendering it reactive thereby. With regard to the traces of oxygen normally present in the mixtures used in the studies of the hydrogen-chlorine combination, no special experiments have been made to ascertain what products result from their presence nor the mechanism of their inhibitory action. Bodenstein[4] assumed that the oxygen was, in some manner, maintained at constant concentration throughout the reaction. This point requires further study in view of the above study with higher concentrations of oxygen. The presence of oxygen, however, even in small concentrations, decreases the length of the chain reactions initiated by the absorbed light, and, as far as present data show, to an extent proportional to its concentration in the hydrogen-chlorine mixture.

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[1] Chapman and co-workers, *J. Chem. Soc.*, 1906, **89**, 1402; 1909, **97**, 845. See also, however, Baly and Barker, *J. Chem. Soc.*, 1921, **119**, 653.

[2] *Ann. Physik*, 1907 (4), **24**, 55, 243.

[3] *J. Chem. Soc.*, 1925, **127**, 787.

[4] *Zeitsch. physikal. Chem.*, 1924, **114**, 208.

*A further insight into the mechanism by which chain reactions are stopped by inhibitors present in small concentrations has been gained by the investigations of Weigert, Coehn and Jung, and Norrish (see *ante*, p 151) on the hydrogen-chlorine reaction The hydrogen-chlorine mixture is only sensitive to visible light in the presence of minute amounts of water vapour The experiments of Norrish indicate that the photo-sensitive reactant is a chlorine water complex, this complex when excited by absorption of radiation is chemically reactive in starting chains This may be due either to an enhanced stability or life of an excited chlorine molecule or to the direct formation of hydrogen chloride according to the reaction $Cl_2H_2O + H_2 \longrightarrow 2HCl + H_2O$ Further experiments are required to elucidate this point In the presence of inhibitors such as ammonia the free water is removed, and on excitation of the remaining chlorine reaction with ammonia takes place; thus inhibition results by stopping the chains from commencing, not from breaking a chain which has already been started

The inhibition of hydrogen-peroxide decomposition —The decomposition which solutions of hydrogen peroxide undergo both thermally and photochemically can be inhibited by suitable additions of selected substances Acids of all kinds, salts such as sodium and calcium chlorides, sodium pyrophosphate, magnesium silicate, alcohols, glycerol, ether, esters, naphthalene, amines, phenols, acetanilide, are typical agents of inhibition[1] The last-named substance has found a considerable technical application for this purpose and possesses a dual efficiency both for the thermal and the photochemical decomposition This dual efficiency is not always obtained The presence of alkalis markedly accelerates the thermal decomposition and inhibits the photochemical decomposition, a factor which is not yet satisfactorily explained

The photochemical studies of the decomposition process have provided the experimental indication that the reaction in question has some type of chain mechanism Henri and Wurmser[2] showed that the light absorption was weak, and that as many as 100 molecules of the peroxide are decomposed for every quantum of light energy absorbed This conclusion has been verified by Kornfeld[3] using monochromatic illumination and exact methods of energy absorption measurements Her results show that the actual number of molecules decomposed per unit of energy absorbed increases with increasing concentration. In solutions 0·016 normal with respect to peroxide, twenty-four molecules decomposed per quantum. In 0 05 normal solutions, the number had risen to seventy-seven molecules. Evidently the chain mechanism becomes more efficient in the more concentrated solutions, or what is the same thing, solvent water molecules break the chains. In acid solutions of the peroxide, the number of molecules decomposed per unit of energy absorbed is markedly lowered. Henri and Wurmser[1] listed a number of inorganic compounds which inhibit the light reaction, and in the following year Mathews and Curtis[2] added a number of organic and inorganic compounds. They failed to observe any properties possessed in common by the inhibitors. Recent investigations by Anderson and Taylor[3] have tended to elucidate the mechanism of certain of these inhibitions. The inhibitory effects exhibited by typical organic compounds of known absorption spectra were examined in four definite spectral regions of the ultra-violet. The inhibition by such agents was associated with the absorption capacity of the compounds for ultra-violet light. A striking correlation between these two factors was obtained in the case of benzene, several esters, acids, amides, ketones, and alkaloids. The inhibitors act more efficiently when in the peroxide solution than when in a screening solution of similar thickness and concentration. This is doubtless to be associated with the existence of the chain reactions already mentioned. These inhibitors act therefore in a twofold capacity. They absorb some of the radiation which might activate hydrogen peroxide molecules. They apparently, also, break whatever chain mechanism may be set up[4] to account for the abnormal photochemical yield. Not all inhibitors act in the former capacity. Certain aliphatic alcohols and amines, halogen, hydroxyl, and hydrogen ions act as inhibitors, although quite diactinic in the ultra-violet. Possibly adsorption of the inhibitor on the active portions of the reaction vessel, resulting in a decrease of the number of chains started, may be found to play an important part in the process.

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[1] For a summary of the photochemical literature see Anderson and Taylor, *J Amer Chem. Soc*, 1924, **45**, 650, 1210 For the literature of the thermal decomposition see Davis, *Chem News*, 1884, **49**, 226, Sabatier, *Bull Soc chim* (2), 1885, **44**, 169, Kingzett, *J Soc Chem. Ind.*, 1890, **9**, 3, *J Soc. Chem Ind*, 1906, **25**, 1219, 1908, **27**, 1214, 1909, **28**, 1314, 1910, **29**, 159, *Bull. Soc Ind. Mulhouse*, 1895, 78, 1897, 95, Clayton, *Trans Farad Soc*, 1916, **11**, 164.

[2] *Compt rend*, 1913, **156**, 1012.

[3] *Zeitsch. wiss. Phot*, 1921, **21**, 66.

Oxidation processes.—It has already been pointed out that in many processes of oxidation the inhibitor may act by removal of a powerful positive catalyst, the oxidation of sodium-sulphite solutions by dissolved oxygen being studied in detail by Titoff. The number of such autoxidation reactions sensitive to inhibitors has been largely increased by various investigations, among which some of the more important are due to Moureu and Dufraisse.[5] Their earliest work showed that the prevention of autoxidation of a variety of substances, for example benzaldehyde and acrolein, was possessed by phenolic compounds. The efficiency of such compounds was remarkable. One molecule of hydroquinine in every 40,000 molecules of acrolein served to make the autoxidation of the latter negligible. Analogous results were obtained with such autoxidisable substances as acetaldehyde, chloral, propionic aldehyde, anisic aldehyde, cinnamic aldehyde, hydrocinnamic aldehyde, furfurol, styrolene, turpentine, linseed oil, nut oil, and butter Furthermore, various secondary phenomena which often accompany autoxidation processes generally related to molecular condensations and manifested by changes of colour, precipitates, change in viscosity, rancidity are also inhibited by such additions Thus, furfurol, instead of turning deep black, remains almost colourless, acrolein no longer yields dis-acryl, a polymerised product, styrolene remains fluid, linseed oil can be exposed in thin layers without losing its fluidity; fatty bodies do not become rancid

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[1] *Compt. rend.*, 1913, **157**, 284.

[2] *J. Physical Chem.*, 1914, **18**, 521.

[3] *J. Amer. Chem. Soc.*, 1923, **45**, 650, 1210.

[4] See Kornfeld, *loc. cit.*, and Nernst and Noddack, *Sitzungsber. preuss. Akad.*, 1923, 112.

[5] *Compt. rend.*, 1922, **174**, 258; 1922, **175**, 127; 1923, **176**, 624, 797; 1923, **178**, 824, 1498, 1861; 1924, **179**, 237.

Further afield, Moureu and Dufraisse have noted the French patent to the Società Anonyma Co-operativa (1905), which claims the protection of silks against light, heat, and atmospheric action by means of thiourea, hydroquinine. and their derivatives, this patent being a product of the investigations of Sisley and Seyewetz,[1] also a German patent (1918) to the Badische Anilin- und Soda-Fabrik claiming the protection of synthetic rubber against autoxidation by the presence of phenolic compounds Gillet and Giot[2] have noted that materials dyed with azo dyes and eosin dyes are protected against colour changes by such inhibitors as Moureu and Dufraisse have studied Rubber oxidation is inhibited by tannin and hydroquinone[3]

Moureu and Dufraisse reject the Titoff concept of suppression of a positive catalyst and have formulated a theory of mechanism which seeks the theoretical solution of the problem of autoxidation in the "peroxidation" of both autoxidant and inhibitor, followed by interaction of the two oxidised agents to regenerate both initial substances and elementary oxygen. Thus, if A be the autoxidisable substance and B be the inhibitor, the sequence of reactions would be

$$A + O_2 = A(O_2), \quad A(O_2) + B = A(O) + B(O),$$

$$A(O) + B(O) = A + B + O_2;$$

or alternatively,

$$A + O_2 = A(O)_2,$$

$$B + O_2 = B(O_2),$$

$$A(O_2) + B(O_2) = A + B + 2O_2.$$

The later papers of Moureu and Dufraisse have been concerned with data designed to prove this mechanism, inhibitors such as iodine and odine compounds, compounds of sulphur and of phosphorus having been studied. They note that most inhibitors are easily oxidisable substances.

It has long been known[4] in connection with induced oxidation processes that, during many processes of autoxidation, for every molecule of oxygen consumed by the substance undergoing oxidation a molecule of oxygen was simultaneously activated and could react to form ozone, hydrogen peroxide, or in the presence of other autoxidisable substances could oxidise them, frequently causing oxidations which cannot be accomplished by ordinary atmospheric oxygen. One such case, studied by Jorissen,[1] is the oxidation of potassium arsenite, present in solutions of sodium sulphite undergoing oxidation. Oxidation of arsenite solutions by dissolved oxygen does not occur. In presence of sulphite, however, equimolecular quantities of the two oxidation products are obtained. In the induced reaction the oxidation of the sulphite is materially lower than in the absence of arsenite. The latter can therefore be regarded as an inhibitor of the sulphite oxidation. Jorissen suggests[2] that the oxidation of a sulphite-arsenite complex occurs. Moureu and Dufraisse have elaborated their theory[3] to explain these cases. Such special explanations cannot have general applicability since it is certain that in many cases oxidation of the inhibitor does not proceed at the same rate molecularly as that of the autoxidisable substance. Furthermore, it would be desirable even in the case of sulphite-arsenite mixtures to ascertain whether the relative amounts of the two oxidised does not vary with the concentrations present.

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[1] *Bull. Soc. chim.*, 1922, 31, 672

[2] *Compt. rend*, 1923, 176, 1402.

[3] *Compt. rend*, 1923, 177, 204. F.P. 509607/1919.

[4] See Chapter VII.

Reasoning from the existence of chain reactions in photochemical processes and from the form of the kinetic equation of a simple bimolecular reaction involving collisions, Christiansen[4] concluded that reactions sensitive to inhibitors, thermal as well as photochemical, might involve a chain mechanism. Reactions in which a minute amount of inhibitor effects a very considerable reduction in reaction velocity would, in such case, be those in which the length of the chain in absence of inhibitor is great, as in the hydrogen-chlorine photoreaction already discussed. There appears to be no ready method of ascertaining whether a purely thermal reaction has a chain mechanism. Photo-reactions, however, can readily be tested by a study of light energy input and chemical reaction which results. If a chain mechanism is established for a photo-reaction it is apparent that the processes succeeding the initial light absorption are not essentially different from thermal processes. If a photo-reaction is shown to have a chain mechanism, it is probable that the same reaction conducted thermally will also involve chains.

From this point of view Taylor[5] and also Bäckstrom[5] have investigated a number of oxidation processes photochemically to ascertain the ratio of light energy input to resultant chemical reaction. Bäckstrom studied both the oxidation of aldehydes such as benzaldehyde and of sodium sulphite. He found in each case that many hundred molecules of the autoxidant react for each quantum of absorbed light energy. Mathews and Dewey [1] and Mathews and Weeks [2] showed that photochemical oxidation of sulphite was sensitive to inhibitors. Pyridine, benzaldehyde, phenol, hydroquinine, ethyl acetate, urea were all retarding agents of varying efficiency. There is, however, some divergence between the thermal and photochemical processes, since copper salts which are powerful catalysts for the thermal process are without action photochemically. The photochemical oxidation of benzaldehyde is retarded by many of the inhibitors of the thermal process. Taylor showed that in the photo-oxidation of an unsaturated glyceride a chain mechanism might also be involved, since the ratio of molecules reacting to quanta absorbed was greater than unity though much smaller than in the cases studied by Backstrom.

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[1] *Zeitsch. physikal. Chem.*, 1897, **23**, 667.

[2] See also *Rec. trav. chim.*,1924, **43**, 582.

[3] *Rec. trav. chim.*, 1924, **43**, 645.

[4] *J. Physical Chem.*, 1924, **28**, 145.

[5] Unpublished experiments.

Young [3] showed that the oxidation of solutions of stannous chloride in water by dissolved oxygen was likewise extremely sensitive to the presence of inhibitory substances. Various alkaloids, mannite, aniline, potassium cyanide, salts of manganese and of chromium were shown to be inhibitors. It is not yet known whether this is an additional case of a reaction involving a chain mechanism. Young showed that it was sensitive to certain positive catalysts present in minute amounts. A concentration of 0·000005 N hydrogen sulphide serves to increase the rate of oxidation by about 25 per cent.

Gaseous oxidations.—Recent investigations have shown that certain gaseous oxidation processes are sensitive to the presence of inhibitory agents. This discovery arose in connection with a study of the explosion of hydrocarbon-air mixtures in the automobile engine. Midgeley [4] has shown that addition of agents, such as iodine, amines, and especially lead tetra-ethyl, to the motor fuel suppresses the tendency to pre-ignition of the explosive mixture in the cylinder, thereby permitting a higher compression to be employed. Corresponding economies in fuel consumption can thereby be secured.

There is no general agreement, as yet, with respect to the function of these added substances in hydrocarbon - air mixtures, various theories having been brought forward.[5] That such substances may act as inhibitors of oxidation was shown by Taylor by demonstrating [6] that lead tetra-ethyl is a powerful inhibitor of the autoxidation of benzaldehyde. On Christiansen's view the mechanism must be one involving a chain mechanism, the energy of the reaction products being transferred to the reactants bringing them into the reactive state, the inhibitor acting by breaking the chains. The view that the explosion reactions involve chains is in harmony with the conclusions of Dixon[1] from his work on the explosion of combustible gas-air mixtures. It is of interest in this connection, also, to record that Humphry Davy[2] made experiments in 1817 on the influence of hydrogen chloride and silicon tetrafluoride on the lower explosion limit of hydrogen. He showed that a mixture of two volumes of hydrogen with one of oxygen did not explode when 2 per cent by volume of hydrogen chloride or 0·8 per cent of the silicon compound was added. Jorissen, Velisek, and Menwissen have recently studied[3] the restriction of the inflammability limits of explosive gas mixtures in presence of various chlorinated hydrocarbons. Further work is needed before the theoretical elucidation of this most important practical problem can be achieved. From such work it may be anticipated that the mechanism whereby the chains are broken will be elucidated. As yet, there is little information on the point. There is some evidence that the inhibitor is oxidised in processes of oxidation. It is also possible that the energy of a "hot" molecule may be dissipated by molecular compound formation with the inhibitor, since, as was shown by Taylor,[4] there is a marked concordance between inhibitory power and ability to form molecular compounds.

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[1] *J. Physical Chem.*, 1913, **17**, 211.

[2] *J. Amer. Chem. Soc.*, 1917, **39**, 635.

[3] *J. Amer. Chem. Soc.*, 1901, **23**, 119, 450.

[4] *J. Ind. Eng. Chem.*, 1923, **15**, 421.

[5] *J. Ind. Eng. Chem.*, 1923, **15**, 421.

[6] A.C.S. Intersectional Meeting, Boston, 1924.

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[1] *Ber.*, 1905, **38**, 2441

[2] *Phil. Trans.*, 1817, 59.

[3] *Rec. trav. chim.*, 1924, **43**, 80, 591.

[4] *J. Physical Chem.*, 1923, **27**, 322.

CHAPTER VII

PROCESSES OF OXIDATION

THE most varied and extensive application of catalysis to the problems of industrial chemistry has been made in the technical development of processes of catalytic oxidation

Catalysts have been successfully employed to accelerate various processes of oxidation extremely dissimilar in character Thus, in processes of surface combustion the catalytic material induces the *complete* combustion of gaseous and vaporised fuels for the production of intense and localised heat, whilst, on the other hand, the incandescent mantle exhibits similar localised combustion for the production of light In those cases also in which the process of oxidation is reversible within the usual temperature range of operation, as in the oxidation of sulphur dioxide to sulphuric anhydride or of hydrochloric acid to chlorine and water, technical development was only possible after the discovery of catalytic agents which would accelerate the processes of oxidation at relatively low temperatures so as to ensure the maximum yield of the desired product at reasonable space velocities.

Another extending field for the technical development of processes of catalytic oxidation is to be found in the cases of *fractional oxidation,* where, by the choice of suitable catalytic material and the proper conditions of temperature, pressure, and concentrations of reacting substances, the reaction is caused to proceed along one path only, with the avoidance of possible side reactions or products of combustion of a higher or lower state of oxidation than is desired Mention may be made of the technical processes for the oxidation of ammonia to nitric oxide, of hydrogen sulphide to sulphur, of methyl alcohol to formaldehyde, and of naphthalene to phthalic anhydride as examples of such fractional oxidation. In all these cases, under adverse conditions, the yield of the desired product may be reduced to nil

Processes of catalytic oxidation may also be *selective* in character. Thus, iron sulphide may be oxidised in the presence of the inflammable constituents of coal gas by the regulated admission of air under suitable temperature control. Mixtures of methane, hydrogen, and carbon monoxide may be analysed by the admission of oxygen, the combustion being conducted in such a manner that, by a suitable choice of catalytic material and operating temperature, only one constituent undergoes oxidation.

The classical experiments of Schönbein on autoxidation, in which the reaction velocity of the process of oxidation is extremely slow, opened up a new and interesting chapter in the theory of combustion. The significance of such processes of cold combustion will at once be apparent from a consideration of the mechanism of the corrosion or rusting of metals and the many remarkable cases of induced chemical reactions which accompany processes of autoxidation.

In the following pages examples are given of the varied and manifold applications of catalysis to these diverse processes of oxidation. It will be noted that, as in many other cases, practice, as exemplified by technical development, has outstripped the theoretical treatment of the subject.

THE MANUFACTURE OF SULPHURIC ACID

The sulphuric acid industry is practically unique in the fact that the two processes employed on an ever extending scale for its manufacture, the so-called " chamber " and " contact " processes, are both catalytic in operation, and in the most modern plants the relative costs of production are practically identical. The " chamber " process, however, is confined to the production of the monohydrate, the maximum strength of acid obtainable being 98 per cent H_2SO_4, whereas the " contact " process is more suitable for the production of " oleum ", *i.e.* sulphuric acid containing varying amounts of SO_3 dissolved in it, pure " oleum " or fuming acid having the composition $2SO_3 . H_2O$ or $H_2S_2O_7$.

The " chamber " process.—In this process the oxidation of sulphur dioxide to sulphuric anhydride by means of atmospheric oxygen is catalytically hastened by oxides of nitrogen, and is one of the very few cases of homogeneous catalysis in a gaseous system.

In actual operation a 6 to 12 per cent mixture of sulphur dioxide in air obtained by passing a regulated amount of air over burning sulphur or sulphides such as pyrites, or spent oxide from gas works, is brought into contact whilst still hot (400°) with a solution of nitrosyl sulphuric acid, by passage through one or two volvic lava- or flint-packed columns termed Glover towers, down which a stream of nitrosyl sulphuric acid is distributed.

The resulting mixture of sulphur dioxide, oxides of nitrogen, and air then pass into a series of leaden chambers into which steam or dilute sulphuric acid is blown by means of suitably shaped nozzles. The earlier rectangular reaction chambers, which would only produce one-sixth of a pound of sulphuric acid per cubic foot in twenty-four hours, are now replaced either by tangential chambers in which nearly 1½ lb. of sulphuric acid can be produced per cubic foot in the same time, or by plate or packed towers in which the oxidation of the sulphur dioxide to the trioxide no longer takes place in the gaseous phase, but in the dilute nitric acid which is added to each tower Although a considerable economy in space is gained in such tower systems, yet the extra installation costs and the increased resistance to the gas passage bid fair to militate against this advantage

The spent gases from the reaction chambers are freed of all residual oxides of nitrogen by passage up a coke or stoneware ball-packed column, the Gay-Lussac tower, down which sulphuric acid is distributed

The weak sulphuric acid from the lead chambers (*ca* 65 per cent) containing both oxides of nitrogen and nitric acid mixed with the nitrous vitriol from the Gay-Lussac tower, is partially concentrated (to 78 per cent) in the Glover tower, where the oxides of nitrogen are removed by the fresh gases and finally brought up to 98 per cent strength by evaporation in Gaillard towers or by means of cascade concentrators

It is evident that under ideal conditions the oxides of nitrogen which are continually returned to the reaction chambers by means of the Glover tower should suffer no diminution during the cycle of operations. In actual practice, however, there is a small but continuous loss of the catalyst equivalent to from 1 to 4 parts of sodium nitrate in 100 parts of sulphur burnt This deficit has to be continuously made good either by the addition of nitric acid to the Glover tower or by supplying oxides of nitrogen to the entering gases In the latter case either small quantities of sodium nitrate (nitre) and sulphuric acid are placed in pots situated in the flue of the pyrites burners, or in the most modern practice, oxides of nitrogen, produced by the catalytic combustion of ammonia (see p 165), are added at the base of the Glover tower

The loss of oxides of nitrogen in the cycle is probably due to a variety of causes, amongst the more important of which may be mentioned

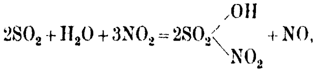
(*a*) The presence of organic matter in the sulphur dioxide—a common occurrence when spent oxide is utilised

(*b*) Loss in the sulphuric acid finally produced and at the exit of the Gay-Lussac tower

(*c*) The reduction of nitric oxide to nitrous oxide or nitrogen by the coke packing in the Gay-Lussac tower, and by decomposition in those parts of the contact chambers where the acid is under 40 per cent strength.

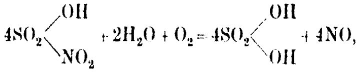
An explanation of the mechanism by which the oxidation of sulphur dioxide to the trioxide is accomplished with the aid of oxides of nitrogen was first suggested by Davy in 1812, as a result of a series of experiments which had been conducted some six years previously by Clément.

and Désormes.[1] It was noted that when insufficient steam was admitted to the reaction chambers white crystals of nitrosulphonic acid were deposited; Davy's hypothesis for the oxidation was based upon the intermediary formation of this acid, according to the following equation:

(1) 

$$2SO_2 + H_2O + 3NO_2 = 2SO_2\left\langle\begin{matrix}OH\\NO_2\end{matrix}\right. + NO,$$

the nitrosulphonic acid reacting with excess of steam and oxygen to form sulphuric acid.

(2) 

$$4SO_2\left\langle\begin{matrix}OH\\NO_2\end{matrix}\right. + 2H_2O + O_2 = 4SO_2\left\langle\begin{matrix}OH\\OH\end{matrix}\right. + 4NO,$$

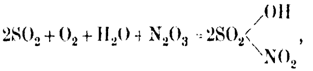
whilst the nitric oxide is reoxidised to nitrogen dioxide as follows:

$$(3)\quad 2NO + O_2 = 2NO_2.$$

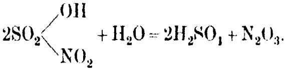
Lunge and Naef in 1881 found, on analysis of the chamber gases in the second and third chambers, that nitric oxide and nitrogen dioxide were present in equivalent proportions, behaving as N_2O_3:

$$(4)\quad NO_2 + NO \rightleftarrows N_2O_3,$$

and suggested the following series of reactions to account for the formation and subsequent decomposition of chamber crystals:

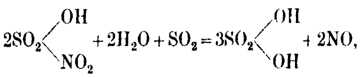
(5) 

$$2SO_2 + O_2 + H_2O + N_2O_3 = 2SO_2\left\langle\begin{matrix}OH\\NO_2\end{matrix}\right.,$$

(6) 

$$2SO_2\left\langle\begin{matrix}OH\\NO_2\end{matrix}\right. + H_2O = 2H_2SO_4 + N_2O_3.$$

In the first chamber the gases are usually colourless owing to a deficiency of nitrogen dioxide. Lunge and Naef suggested that the removal of this constituent was taking place by means of a side reaction, as follows:

(7) 

$$2SO_2\left\langle\begin{matrix}OH\\NO_2\end{matrix}\right. + 2H_2O + SO_2 = 3SO_2\left\langle\begin{matrix}OH\\OH\end{matrix}\right. + 2NO,$$

which would thus explain the presence of the nitric oxide in excess of the equivalent proportions demanded by Equation (4). These comparatively simple reactions, according to Raschig[2] and Trautz,[3] are not a sufficient explanation for all the phenomena observed when sulphurous or sulphuric acids are agitated with oxides of nitrogen. It is comm knowledge that in the usual nitrometer estimations a purple or pi coloration is nearly always present towards the end of the reaction.

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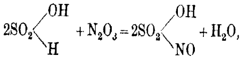
[1] See Lunge, vol. i.; Raschig, *J. Soc. Chem. Ind.*, 1907, **10**, 965: 1911, **30**, 106; Partington, *The Alkali Industry*, 1918.

[2] *Annalen*, 1887, **241**, 200.

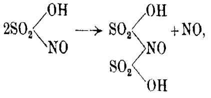
[3] *Zeitsch. physikal. Chem.*, 1888, **2**, 608.

The composition of the purple acid is unknown, but in all probabili contains the nitroso-group, NO, to which its colour may be attribute

Trautz postulates the formation of an unstable nitrosulphonic ac according to the following reactions :

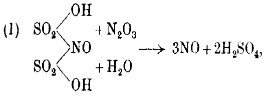


$$2SO_2{<}^{OH}_{H} + N_2O_3 = 2SO_2{<}^{OH}_{NO} + H_2O,$$

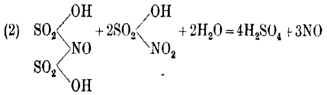


$$2SO_2{<}^{OH}_{NO} \longrightarrow \begin{array}{l}SO_2{<}^{OH}_{NO}\\ SO_2{<}_{OH}\end{array} + NO,$$

which is subsequently decomposed according to the following two side reactions.

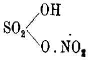


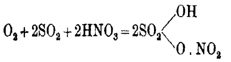
$$(1)\quad \begin{array}{l}SO_2{<}^{OH}_{NO} + N_2O_3\\ SO_2{<}_{OH} + H_2O\end{array} \longrightarrow 3NO + 2H_2SO_4,$$



$$(2)\quad \begin{array}{l}SO_2{<}^{OH}_{NO}\\ SO_2{<}_{OH}\end{array} + 2SO_2{<}^{OH}_{NO_2} + 2H_2O = 4H_2SO_4 + 3NO$$

The existence of a hypothetical nitrosulphuric acid $SO_2{<}^{OH}_{O.NO_2}$ has also been suggested by Lunge, formed by the interaction of nitric acid vapour on sulphur dioxide in the presence of air.





$$O_2 + 2SO_2 + 2HNO_3 = 2SO_2{<}^{OH}_{O.NO_2}$$

It must, however, be admitted that our knowledge of the various side reactions which may occur between the oxides of nitrogen catalysts and the oxides of sulphur is far from complete, but it appears probable that the explanation advanced by Lunge and Naef represents the most important sequence of actions taking place under the conditions in actual chamber practice

The "contact" process.—The early development of the lead chamber process for the manufacture of sulphuric acid took place in the years 1740 and 1750.

In 1812 Davy, who was the first to point out the true function of the oxide of nitrogen in the oxidation of sulphur dioxide, suggested the possibility of using platinum sponge as a catalyst for the same purpose. Phillips, in 1831, may claim to have been the pioneer in testing Davy's suggestion on the industrial scale, but owing to the rapidity with which his catalytic material became poisoned the process was abandoned until 1875, when Squire and Messel succeeded in making the process a technical success for the production of "oleum". These investigators utilised pure gases obtained by the decomposition of sulphuric acid on hot brick surfaces or by the combustion of sulphur, the sulphur dioxide being subsequently purified by washing with water under pressure.

The rapid development in the contact process during the opening years of the present century is chiefly due to the work of Kneitsch and Krauss,[1] who carried out a very systematic investigation on the reaction velocities and the conditions of equilibrium of the reaction

$$2SO_2 + O_2 \rightleftarrows 2SO_3,$$

which was found by C. Winckler to be a reversible one. It was shown that the value of the equilibrium constant

$$K_p = \frac{P_{SO_3}}{P_{SO_2}\sqrt{P_{O_2}}},$$

where P_{SO_3}, P_{SO_2}, and P_{O_2} are the respective partial pressures of the reacting constituents, decreased with rising temperatures, as is observed from the following figures:

Temperature.	K_p.	Temperature.	K_p.
430°	198·0	600°	14·9
450	187·7	610	10·5
500	72·3	627	5·5
528	31·3	700	4·8
553	24·1	727	1·8

By means of the general equation

$$\frac{d \log K_r}{dT} = -\frac{Q_r}{RT^2},$$

assuming that the value of Q_r, the heat of reaction, which according to Berthelot and Bodenstein[2] is equal to an evolution of 21,700 cals. at the ordinary temperature, does not change seriously in value over the temperature range, we can calculate the value of K_r, and hence that of K_p, for any desired temperature. The value of the integration constant can be obtained by taking an experimentally found value of K_p or by means of Nernst's heat theorem.

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[1] *Ber.*, 1901, **34**, 4069.

[2] Bodenstein and Finck, *Zeitsch. physikal. Chem.*, 1907, **60**, 1, 46.

The fractional conversion, i.e. the values of the ratio $\frac{SO_3}{SO_2+SO_3}=x$ could consequently be calculated when the magnitude of K_p had been determined It is easy to show that the percentage conversion $100\,x$ is equal to

$$100\sqrt{P_{O_2}}\,\frac{K_p}{1+K_p\sqrt{P_{O_2}}}$$

From this equation it is a comparatively simple matter to calculate the composition of the gas as it comes from the contact material in which equilibrium has been established, whilst the calculation of the final composition from an analysis of the entering gases can be made by means of the following equation

$$100\,x=100\,\frac{K_p}{K_p+\frac{1}{\sqrt{\frac{b-0{\cdot}5\,ax}{100-0{\cdot}5\,ax}}}},$$

where a and b are the percentages of sulphur dioxide and oxygen in the initial mixture

From these equations the following interesting facts can be deduced first, that the ideal catalyst should be active at low temperatures, preferably below 500°, where the values of K_p are large, secondly, although an increase in the partial pressure of oxygen is beneficial in that it tends to raise the value of x nearer to unity, yet a limit is set to the quantity of air admitted by the effect of the diluent nitrogen. If we assume a mere trace of sulphur dioxide to be present in entering gases, i.e. a is approximately zero and $b=20{\cdot}9$ per cent, then

$$\sqrt{\frac{b-0{\cdot}5\,ax}{100-0{\cdot}5\,ax}}=\sqrt{\frac{b}{100}}=0{\cdot}457,$$

i.e.
$$100\,x=100\,\frac{K_p}{K_p+2{\cdot}2}$$

For large values of K_p the yield is practically theoretical, but at 700° the value of $100\,x$ has sunk to 60 in spite of the very large quantities of oxygen present, whereas if no nitrogen had been present at all the value of $100\,x$ approximates to $\frac{100\,K_p}{K_p+1}$, or 83 at 700°. The optimum results are obtained when the quantity of excess air admitted to the pyrites burners raises the oxygen content to the ratio $SO_2 : O_2 :: 2:3$, or three times the theoretical amount for complete conversion to the trioxide.

Having determined the conditions governing the oxidation of the sulphur dioxide, Kneitsch and Krauss investigated the reaction velocity in the presence of different catalytic materials Utilising purified technical converter gas of the following composition: 7 per cent SO_2, 10 per cent O_2, and 83 per cent N_2, the speed of conversion was determined when passed over various catalysts at different speeds and varying temperatures. In Fig. 8 (Curves I and II) are shown the results of passing such a gas mixture over platinised asbestos in a porcelain tube at varying temperatures; it will be noticed that conversion with this, the most efficient of all the catalysts yet investigated, commences at 200° with a flow rate of 300 c.c. per minute (Curve I) and at a little under 300° with a flow rate of 20,000 c.c. per minute (Curve II), and as the flow rate increases a higher reaction velocity is required, necessitating a higher temperature with a corresponding reduction in the equilibrium concentration of sulphuric anhydride obtainable. Curve III indicates the loci of the maxima of a set of the curves, utilising identical catalytic material, platinised asbestos and converter gas of similar composition but with different rates of passage.

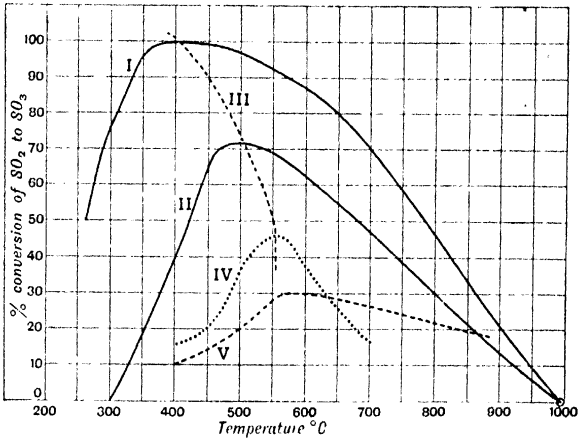

Fig. 8.

It is evident that if some circulating system were employed, or alternatively a series of catalytic tubes were so arranged that the sulphur trioxide formed was removed after each catalytic treatment, the maximum conversion per unit of time would not be obtained with an operating temperature and speed of passage corresponding with the probable maximum conversion, but would entail a very high rate of passage with a relatively low conversion, the speed and temperature being so adjusted as to ensure the product, per cent conversion × flow rate being a maximum Technical difficulties associated with the removal of the sulphur trioxide from a gas containing relatively large quantities of the lower oxide appear to have prevented the realisation of this possible procedure.

Curve IV indicates the results obtained with burnt pyrites (CuO,Fe_2O_3) as contact material with a flow rate of 500 c c per minute, whilst Curve V shows the low duty obtained with broken porcelain as catalytic agent.

We have already referred to the employment of purified converter gas by several investigators. Squire and Messel appear to be the first to have realised the significance of catalyst "poisons" in the ordinary gas, and used, as an alternative, sulphur dioxide prepared from some purer source. The Badische Anilin- und Soda-Fabrik successfully solved the technical problem of purifying ordinary converter gas from poisons, notably arsenic, antimony, phosphorus, and lead, by steam treatment, cooling, and washing. The resulting gas is so purified as to be optically pure, showing complete freedom from suspended matter even when subjected to intense illumination

Since the optimum conversion temperature lies between 400° and 450°, it was evident that for the successful technical development of the process the entering gases should strike the catalyst at a temperature approximating as nearly as possible to this, and should leave the catalyst at sensibly the same temperature. The reaction, however is strongly exothermic, 21,700 cals being evolved per grm -mol of sulphur dioxide converted The Badische converter was accordingly constructed of relatively narrow iron reaction tubes, 10 per cent platinised asbestos being employed as catalytic material The maximum radiation was thus obtainable by this method A part of the inflowing gas, passing externally over the tubes in a counter-current direction, was so adjusted as to regulate the catalyst temperature, and at the same time assisted in heating up the remainder of the entering gases

In the Mannheim process developed by Clemm and Hasenbach a preliminary conversion is effected by passage of the gases over burnt pyrites at from 500° to 600° where some 45 per cent conversion is effected The gases freed from the sulphuric anhydride by absorption in strong sulphuric acid are then passed on to the lower temperature platinum catalyst A dual advantage is thus obtained. In spite of the lower duty obtained with the burnt pyrites catalytic material on account of the somewhat elevated reacting temperature, this catalyst is not so sensitive to traces of poisons as the platinum and is a comparatively cheap material to utilise. As a further consequence, a very pure gas passes on to the platinum converter, and since nearly half of the sulphur dioxide has already been removed, the temperature of this catalyst can be easily adjusted within the prescribed limits.

Of the various catalytic materials employed to accelerate the oxidation of sulphur dioxide to sulphuric anhydride, platinum is undoubtedly the most active, and much ingenuity has been displayed in obtaining the maximum yield possible with the aid of relatively small quantities of this somewhat expensive material.

In the Badische type of plant where platinised asbestos is utilised, the platinum is frequently deposited from the platinic chloride by means of a formate solution according to the method originally suggested by Loew.[1]

The Tenteleff process utilises a series of coarse asbestos string mats some 2 feet by 3 feet in area, impregnated with platinum black, from twelve to twenty-five being used as the contact mass; the quantity of platinum distributed on each mat varies from 60 to 65 grms.

The Schröder-Grillo contact material[2] is undoubtedly the most ingenious of any which are in operation, producing a very active form of platinum black and at the same time exposing a large area of catalytic surface.

Partially calcined magnesium sulphate is sprayed with a solution of platinum salt and heated up in the presence of sulphur dioxide, the reduction of the platinum being thus effected. From 0·2 to 0·3 per cent of platinum on the magnesium sulphate is sufficient to form an excellent contact material. With 5 grms. of platinum one ton of "oleum" can be produced per day with a loss of only 20 mg. of metal.

Of the various other catalytic materials suggested, it seems that only burnt pyrites has actually been used on an industrial scale. By reference to the patent literature, the problem of finding some other non-platinum catalyst more active than burnt pyrites is still the object of investigation. Amongst the more important materials suggested may be mentioned the oxides of copper, vanadium, uranium, chromium, nickel, and cobalt, frequently incorporated with aluminium, beryllium, zirconium, or zinc oxides, or the rare earths, such as didymia or ceria; thus vanadium pentoxide when precipitated in a fine state of subdivision on silica is stated to be as effective as platinum.[3] It is of interest to note that oxide of arsenic itself, although a poison for platinum, is a comparatively good catalyst at somewhat higher temperatures.[4] Water, on the other hand, inhibits the reaction very strongly by selective adsorption even up to 700° C. More novel is the suggestion to incorporate with the catalytic material some body which readily absorbs sulphur trioxide at the temperature employed, and disengages it again at a higher temperature.

Various theories have been put forward to explain the mechanism of the contact process; it is usually assumed that the intermediary formation of the platinum oxide, PtO, or the more transitory and possibly hypothetical dioxide, PtO_2, suggested by Wöhler and Engler,

[1] *Ber.*, 1890, **23**, 289.
[2] *J. Soc. Chem. Ind.*, 1903, **22**, 348.
[3] G.P. 291792 of 1913.
[4] Lunge and Reinhart, *Zeitsch. angew. Chem.*, 1904, 1014; Koeppler, *ibid.*, 1908, 532.

plays the important rôle in this catalytic operation, according to the following cycle

$$\text{(i)}\quad 2Pt+O_2 \longrightarrow 2PtO+2SO_2 \longrightarrow 2Pt\ \ 2SO_3.$$

$$\text{(ii)}\quad Pt+O_2 \longrightarrow PtO_2+2SO_2 \longrightarrow Pt\ \ 2SO_3$$

Wieland, however, has laid stress on the "hydration" theory of chemical action Since perfectly dry sulphur dioxide and oxygen do not combine, he represents the oxidation of the sulphur dioxide as subsequent to a previous hydroxylation

$$SO_2+H_2O \longrightarrow H_2SO_3,$$
$$H_2SO_3 \longrightarrow SO_3+H_2,$$
$$2H_2+O_2 \longrightarrow 2H_2O.$$

It may be urged in favour of this view that in those cases where intermediate products of oxidation can be isolated and analysed—especially in organic reactions where the hydroxyl groups can be fixed and characterised as soon as they are formed by the substitution of a suitable non-reactive grouping—the evidence for hydroxylation as a stage in oxidation is remarkably strong

It is extremely probable that adsorption phenomena exert a by no means inconsiderable influence on the rate of the reaction

With oxide catalysts such as oxide of iron it is generally assumed that the formation of an intermediary sulphate occurs according to the following cycle

$$\begin{tikzcd}
2Fe_2O_3+6SO_2+3O_2 \arrow[r] & 2Fe(SO_4)_3 \arrow[d, dashed, no head] \\
2Fe_2O_3+6SO_3 \arrow[u, bend left] & \arrow[l, dashed]
\end{tikzcd}$$

It is evident, however, by reference to the list of oxides suggested as suitable for technical processes, that practically only those elements are included which possess at least two oxides, and, as in many other catalytic processes, we are equally justified in assuming the catalytic activity to be due to an oscillation between the two states of oxidation

$$\begin{tikzcd}
Fe_2O_3+SO_2 \arrow[r, dashed] & 2FeO+SO_3 \arrow[d, "+O_2"] \\
\arrow[u, dashed] & Fe_2O_3, \arrow[l, dashed, no head]
\end{tikzcd}$$

$$\begin{tikzcd}
CeO_2+SO_2 \arrow[r, dashed] & CeO+SO_3 \arrow[d, "O_2"] \\
\arrow[u] & CeO_2 \arrow[l, dashed, no head]
\end{tikzcd}$$

It must also be admitted that the explanation formed on the "intermediary sulphate" theory is not very satisfactory in the light of the researches of Bodenstein and Suzuki,[1] who showed that the first products of the distillation of ferric sulphate are SO_2 and O_2, which then react in the presence of ferric oxide to produce SO_3, whereas SO_3 should be the primary product on this hypothesis.

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[1] *Zeitsch Elektrochem.*, 1910, **16**, 912

Use of catalysts in the Hargreaves process.—Hargreaves and Robinson in 1870 introduced a method for the manufacture of salt cake (Na_2SO_4) by the interaction of pyrites burner gas and air on hot salt at 525°.

Above 600° fusion of the salt occurs, thus setting a limit to the temperature for the reaction. To accelerate the reaction at low temperatures, various catalysts have been proposed, notably ferric oxide[1] and copper oxide.[2]

It was suggested that the salt should be moistened with a solution of the sulphate of the metal so as to obtain an activated salt containing from 0·1 to 1·0 per cent of the metal.

The experimental investigation of the influence of copper and iron salts was reported by Conroy.[3] The conclusions reached are thus summarised. Salt is decomposed by a mixture of sulphur dioxide and air at a temperature below 600° to yield sulphate and chlorine. Decomposition in glass vessels is exceedingly slow. With addition of 0·25 per cent of copper in the form of sulphate, reaction begins at 400° and increases in amount with temperature.

The rate of action at 600° was roughly 50 per cent greater than at 450°. Increased concentration of copper increased the rate of reaction. It was shown that 0·5 per cent of iron as sulphate was catalytically equivalent to 0·25 per cent of copper. Magnesium and aluminium sulphates were without action. With suitable gas speed, reaction was quantitative, all sulphur dioxide being retained. At higher speeds of passage, both chlorine and sulphur dioxide escaped The conversion to sulphate could be carried to completion.

In Conroy's view, the salts of copper and iron probably act by inducing the combination of sulphur and oxygen to form sulphuric anhydride, since, by inserting platinised asbestos in the inlet end of the reaction tube the ratio of the chemical equivalents of chlorine to sulphur dioxide and sulphur trioxide rose from 1 : 14 to 1 : 1. This method of working the process, viz. by passing a mixture of sulphur dioxide and air through vessels containing alternately a contact substance to produce sulphuric anhydride and salt, was patented by Deacon in 1871.[4]

To check fusion, Clemm proposed[5] to admix clay with the salt, utilising copper oxide or ferric oxide to aid the reaction.

THE OXIDATION OF AMMONIA TO NITRIC ACID

After the war the national interests, the increasing demand for nitric acid for growing industries in the various branches of organic

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[1] Hargreaves, 1886.

[2] Kruhing and Dernoncourt, 1897; Clemm, 1899; and Hargreaves, 1907

[3] *J Soc. Chem. Ind.*, 1902, **21**, 304.

[4] B.P. 1908/1871.

[5] B.P. 15152/1899.

chemistry and as nitrates for fertilisers, as well as the rapid strid
recently made in the economic production of ammonia both as
coal by-product and in the form of cyanamide and pure ammoni
manufactured by the various synthetic processes, have all tende
to make the technical operation of an ammonia oxidation plan
not merely a war industry but an integral part of the economi
development of the State.

The pioneer work on this problem was accomplished by the French industrial chemist, Kuhlmann, in 1839, but until Ostwald and Brauer published their researches in 1903 no progress was made in the technical development of the process

During the last few years several systems have been developed on an industrial scale, yielding on an average an efficiency of conversion of from 90 to 95 per cent Amongst the more important may be mentioned those of Ostwald and Brauer, Frank and Caro, and that of Kaiser Modifications and improvements of these German processes have been developed by the Allied Government Research Departments and by private firms during the period of the war, effecting a combination of the best features of the respective plants

The oxidation of ammonia is effected by the passage of an air-ammonia or oxygen-ammonia mixture over a catalytic material maintained at a suitable temperature

The oxidation may take place in two ways the reaction of decomposition,

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O + 301{,}000 \text{ cals},$$

and the reaction catalytically accelerated,

$$4NH_3 + 5O_2 = 4NO + 6H_2O + 215{,}000 \text{ cals}$$

Under the conditions of catalytic combustion the oxidation of ammonia is practically complete, as can be calculated from the Nernst heat theorem, assuming that the above equation is strictly reversible

The heat liberated in the combustion of 4 molecules of ammonia under the above conditions is 215,000 cals at 17°. For a homogeneous gas reaction we can calculate from Nernst's equation the equilibrium constant

$$K_p = \frac{p_{NH_3}^4 \times p_{O_2}^5}{p_{NO}^4 \times p_{H_2O}^6},$$

$$\log_e K_p = \frac{Q_0}{RT} + \frac{\Sigma \nu C_{0_p}}{R} \log_e T + \frac{\Sigma \nu \beta}{R} + \Sigma \nu i,$$

where Q_0 and C_{0_p} are the heat of reaction and the specific heats of th
reactants at absolute zero, $\Sigma\nu$ the algebraic sum of the number o
molecules, and i the integration constant of the vapour pressure formula

For C_{0_p} we can approximate the value 3·5 given by Nernst. Th
chemical constants for O_2, NH_3, NO, H_2O are 2·8, 3·3, 3·5, and 3·

respectively, and $\Sigma\nu i = -8{\cdot}4$. Correcting the heat of combustion, viz. 215,000 for a temperature of absolute zero, taking into account the change in the specific heat of the gaseous constituents with the temperature, Q_0 will be found to be equal to 216,300 cals.

For temperatures of oxidation between 500° and 1000°, the range usually adopted in technical plants, or a mean of 800°, $C_p = C_{0_p} + 2\beta T$.

$$2\beta = \frac{C_{p,800^\circ} - 3{\cdot}5}{800}.$$

Hence $$\log_{10} K_p = \frac{216{,}300}{4{\cdot}57\,T} - 1{\cdot}75 \log T + \frac{0{\cdot}007}{4{\cdot}57}\,T - 8{\cdot}4.$$

For log K_p we find :

T.	$\log K_p$.
500°	−108
800	− 71
1000	− 61

It will be observed that even at 1000° the quantity of ammonia in equilibrium with the nitric oxide under these conditions is almost vanishingly small and quantitative yields should always result.

In practice, quantitative yields are never obtained, for the following reasons :

(1) The time of contact of the air, or oxygen-ammonia mixture with the active surface of the catalyst may be too long. Under these conditions the nitric oxide formed by combustion with the ammonia will commence to dissociate and establish equilibrium, according to the equation

$$2NO \rightleftarrows N_2 + O_2.$$

This equilibrium is likewise governed by the temperature of the gas and is the basis of the arc process of fixing atmospheric nitrogen.

According to Nernst and Haber, the equilibrium amount of nitric oxide formed in air at 2000° is only 1·0 per cent varying to 10 per cent at 4140°, but is practically negligible at the working temperatures of the ammonia oxidation process (*circa* 0·001 per cent NO at 800°). On the other hand, the velocity with which equilibrium is established is greatly increased by a rise in temperature, and the gas containing the high concentration of the nitric oxide produced by combustion of ammonia must be rapidly cooled to decrease the velocity of the normal decomposition. It is evident from this consideration that the catalyst should be maintained at a low temperature and that the period of contact of the gases with the catalyst be as short as possible.

(2) Part of the ammonia may escape contact with the catalyst. Undecomposed ammonia present in the effluent gases will react with the nitrous acid formed on the condensation of the nitrogen oxides in water, with the liberation of nitrogen :

$$NH_3 + HNO_2 = N_2 + 2H_2O.$$

Twice the amount of nitrogen originally present in the escaping ammonia will thus be lost

(3) Partial direct combustion to nitrogen may occur

Ostwald and Brauer's process.—This system has been largely developed in Germany, whilst independent factories were established by the Nitrogen Products Co at Vilvorde in Belgium, Angoulême in France, Dagenham in England, and at Legnano in Italy As catalytic material, platinum foil is used in the form of a corrugated roll, about 2 cm deep, 50 grms in weight, loosely inserted in the end of a nickel tube some 2 metres long, and 9 cm in diameter (solid drawn nickel is said to be preferable to welded tube) The nickel tube through which the ammonia and air mixture (*circa* 5 per cent NH_3) passes is enclosed by an enamelled iron tube somewhat wider in diameter, the whole system thus acting as a simple form of heat interchanger The ammonia-air mixture is thus heated up to a temperature of 650° before striking the platinum roll, which is maintained at 650°-700° by the heat of combustion of the ammonia The flowing gases, consisting of nitric oxide, nitrogen, and residual oxygen from the air, which is added in excess, are cooled down, and, after sufficient time of storage to ensure that the oxidation of the nitric oxide to nitrogen dioxide is complete, are passed into the nitric acid absorption towers

Frank and Caro's process.—The disadvantages of the original process, namely, the lack of control of the catalyst temperature and the relatively large amount of platinum required to produce a given quantity of nitric acid (50 grms will only produce some 30 tons per annum), led Frank and Caro to construct a form of converter in which a more economical utilisation of the catalyst (in this case platinum also was used) was attempted

The converter of rolled aluminium consisted of a rectangular column containing baffle plates equally spaced and terminated by a conical hood of the same material A fine platinum gauze (80 linear meshes to the inch of wire 0 0026 inch diameter) was stretched across the converter column, and by means of silver leads could be maintained at a uniform temperature (*circa* 650°) by the passage of an electric current With the catalytic material in this form a somewhat richer air-ammonia mixture (9 11 per cent) could be dealt with and the converters constructed in considerably larger sizes Technical units have been constructed up to 1 square foot in cross-section, whilst in America experiments on still larger units have been carried out The output per square foot of catalyst surface is approximately 700 kilogrms of nitric acid per 24 hours, whilst the weight of platinum is less than 40 grms per square foot The yield is stated to average 92 per cent

Kaiser's process.—From 1911 to 1916 Dr Kaiser, as a result of nvestigations carried out on a technical scale at Spandhau, near Berlin, put forward somewhat startling claims for a process developed by him.

In this process the single layer of platinum gauze is replaced by four separated layers of similar material, the total thickness not exceeding 0·5 to 0·6 mm. Electrical heating is dispensed with, and the air previous to admixture with the ammonia is preheated by means of a coke fire to 300°-350°. Kaiser's original claims of efficiencies, exceeding 100 per cent owing to the simultaneous autoxidation of atmospheric nitrogen, have now been shown to be fallacious, and it appears possible that these were advanced only to overcome certain difficulties attached to the patent protection of his process.

The process was installed in a somewhat modified form by Saposhnikoff at Kharkoff in Russia, where an overall efficiency of over 92 per cent has been claimed. Recent experiments have also indicated that higher rates of gas flow and a consequent greater output per square foot of converter area are obtainable with multiple gauzes, although the actual output per grm. of platinum is somewhat lower. The average yield per square foot of converter area with two gauzes per 24 hours is 1·5 to 1·8 metric tons of nitric acid (in all cases calculated as 100 per cent).

Small plants using two or more gauzes are already installed in England for the supply of oxides of nitrogen in vitriol chambers and are giving 95 per cent yields continuously.

In modern plants preheating of the gas mixture is employed. It is found that the optimum temperature of the platinum gauze is *ca.* 1100°C. Taking the mean specific heats of the products of oxidation as follows:

$$N_2 = 6{\cdot}88 \quad O_2 = 4{\cdot}00 \quad NO = 7{\cdot}50 \quad H_2O = 9{\cdot}20,$$

the heat content of a 1 : 11 NH_3 air mixture after combustion will be

$$[8{\cdot}69N_2 + 1{\cdot}06O_2 + 1{\cdot}5H_2O + NO]\,T = 85{\cdot}8\,T.$$

Hence, since the final temperature must be 1100° C., and since 54,000 cals. are evolved per grm.-mol. of ammonia burnt, we obtain

$$1100 - \frac{54{,}000}{85{\cdot}8} = 360°\ C$$

as the optimum temperature of preheating.

A modern form of technical converter unit shown in the illustration (Fig. 9) is described by Partington[1] as follows: It consists of a top and bottom cone, with three rectangular body pieces between them, all in cast aluminium ⅕ inch thick, the rectangular area exposed measuring 4 inches by 6 inches. The pieces are provided with flanges, ¾ inch wide, to facilitate bolting together, and three perforated baffles are inserted in all the junctions except that between the top cone and the top segment of the body, which is occupied by the catalyst frame. Though each cone possesses a sight orifice, 1½ inch in diameter, for reasons of standardisation, that in the top cone alone is used, and is provided with a mica window for inspection of the catalyst. Aluminium bends of 2 inches internal bore provide inlets and outlets for the mixture

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[1] *J. Soc. Chem. Ind.*, 1918, **37**, 337.

of air and ammonia at the bottom, and the oxides of nitrogen at the top, respectively. The overall length of the converter is about 4 feet and its weight is about 32 lbs.

The air supply is obtained from a blower, and it is essential that the air and ammonia should be well mixed. If ammonia gas is used, it may be injected into the air stream through a nozzle, after both gases have been measured. In technical practice it is more convenient to use purified ammonia liquor containing 25 per cent of ammonia, which is now a commercial article. The air is passed, together with a small amount of steam, into the base of a coke tower down which this liquor flows. The mixed gases are cooled in the upper portion of the tower, where the steam is condensed. The mixture of air and ammonia should be filtered, either by passage through a length of coke packing in the upper portion of the tower or through a filter packed with glass wool, which removes particles of dust. Oxide of iron particularly must be eliminated, as this has a deleterious effect on the platinum catalyst.

The most important part of the apparatus is the catalyst, which is fixed between the upper cone and body segment. It consists of one or more gauzes made of pure platinum wire, stretched across the converter at right angles to the gas flow. The wire used is 0·0025 inch in diameter, and is woven into gauze with 80 meshes to the inch. The gauzes are mounted in an aluminium frame. The reaction occurs during the very small interval of time in which the gases are in contact with the catalyst.

The operation of the catalyst must be initiated by heating the gauze, either by means of a non-luminous gas flame or by heating electrically with suitable current conducted through leads attached to the opposite edges of the gauze. When the first method is used, an orifice is provided in the upper body segment just below the gauze, which admits of the introduction of the flame, and is closed when the converter is in operation. The converter figured is provided with leads for electric current. When the reaction begins, the gauze is maintained at a red heat by the heat of oxidation, and the conversion proceeds uninterruptedly as long as the supply of air and ammonia is maintained. The platinum gauze may be used for about three months, after which it is desirable to replace it by a new gauze and to clean and refit. New gauzes are not very active at first, but acquire their full catalytic activity after a few hours' running.

THE CATALYSTS EMPLOYED IN THE OXIDATION OF AMMONIA

Platinum.—It will be noted that all existing technical ammonia oxidation plants employ platinum [1] as a catalyst, and many interesting observations have been made as to the catalytic activity of platinum for this purpose Kuhlmann, in 1839, first noted that platinum sponge was more efficient than platinum black for the production of oxides of nitrogen, but that larger yields of nitrogen were obtained with the latter Bright platinum is scarcely active Ostwald and Brauer[1] continued Kuhlmann's researches and showed that the optimum results were obtained when bright platinum was coated with an almost invisible film of grey or black platinum and that only a short period of contact was necessary, *i.e* 0·01 second Schick, in 1907, noted that platinised porcelain, of which the glaze was slightly fusible, permitting the coalescence of the platinum into minute droplets, was extremely active, and recent photomicrographic investigation of platinum gauze also indicates that there is a gradual increase in catalytic activity associated with the formation of minute craters on the metal, the lip of each crater being just tinged with "grey" or "black" platinum By the use of such an active net the period of contact may be reduced to as low a figure as 0·0006 second. The illustrations (Fig 10) given show the changes in structure of a gauze during use

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[1] Recent information from Germany indicates that the use of non-platinum catalysts has been largely developed during the last two years.—E. K. R.

It seems probable that the black or grey platinum is the active catalyst, but when present in large quantities it is liable to cause the formation of nitrogen either in the primary oxidation of the ammonia, or, as seems more probable, due to secondary decomposition of the nitric oxide

Poisons.—Small quantities of hydrogen sulphide rapidly poison the catalyst, but when the impure gases are replaced by purified ammonia-air mixtures a partial recovery of the poisoned catalyst always results In the other cases of poisoning this process is, however, quite irreversible As an example the following data for acetylene poisoning may be noted

Time Minutes	Per cent yield	Volume per cent Acetylene
0	93·0	0
		Added 0·44
20	92·8	,,
26	91·4	,,
32	87·8	,,
38	72·3	,,
	Impurity removed	
78	71·9	
200	71·4	

Whilst both hydrogen sulphide and acetylene are removed from the platinum surface and thus do not effect poisoning by covering the surface, they effect a partial fusion and crystallisation of the surface and thus diminish the catalytic activity

Phosphine exerts a marked partially reversible poisoning action, a content of only 0·00002 per cent by volume will reduce the yield by no less than 20 per cent On recovery a net yield of 80 per cent as compared with an original of 93 per cent can be obtained.

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[1] *Chem Zeit*, 1903, **27**, 100.

taining as impurity 0·38 per cent C_2H_2 and 0·0002 per cent PH_3 will reduce the yield from 93 to 70 per cent in one hour On the addition of 0·02 per cent of H_2S the yield commences to rise and will reach 86 per cent in less than two hours

Non-volatile impurities, *e g* silica, ammonium phosphate, dust, oxide of iron, and the like, must naturally be rigorously excluded Probably for this reason platinum impregnated on pumice or asbestos has a remarkably low efficiency

Non-platinum catalysts. Kuhlmann, in 1839, noted the catalytic activity of oxides of copper, iron, and nickel for this purpose, whilst Du Motay [1] proposed the use of alkaline manganates, permanganates, bichromates, and plumbites

Ostwald and Brauer, in the series of researches previously alluded to, indicated the activity of the oxides of manganese, lead, silver, copper, chromium, nickel cobalt, vanadium and molybdenum, but stated that they were all inferior to platinum in catalytic activity Frank and Caro [2] proposed the use of ceria and thoria, whilst Wendriner suggested the black oxide of uranium, U_3O_8

During the period of the war, research in the utilisation of non-platinum catalysts has been extremely active, especially in America and Germany, where the dearth of platinum was somewhat acute Although no non-platinum catalytic process has been assured of technical development,[3] nevertheless the results obtained on a small scale are sufficiently encouraging to justify their continuance

Jones and Morton in the United States have reinvestigated Du Motay's alkaline plumbites, especially those of magnesium zinc cadmium and aluminium, with success Their reactivity towards metals and all forms of glass and silica at high temperatures is the chief objection to their use

In England, Maxted [4] has investigated the use of oxides of iron admixed with certain promoters such as copper oxide, lime, or bismuth oxide He has shown that the conversion of ammonia-oxygen mixtures can be accomplished in heated tubes, specially activated on the inside, with more than a 90 per cent efficiency The short life of the catalyst under these conditions is the chief drawback to his process The use of oxygen instead of air is obviously only permissible in conjunction with a synthetic ammonia plant in which the oxygen fraction from the liquid-air plant used in the preparation of the nitrogen would be available

The Badische firm in Germany have investigated the effect of a great number of promoters on active or feebly active catalysts, such as tellurium and lead oxides on platinum, bismuth, chromium, and cerium oxides on iron oxide

The yields under approximately identical conditions for a number of such mixed oxide catalysts are given in the following table

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[1] B P 491,1871

[2] D R P 234329

[3] See *ante*, p 170

[4] *J Soc Chem Ind*, 1917, **36**, 777

Mixed oxides of	Per cent yields	Mixed oxides of	Per cent yields.
Fe	83·5	FeSb	82·5
FeBi	94·6	FeUr	82·0
FeCu	92·0	FePb	89·8
FeCe	90·0	FeMn	79·0
FeW	89·3	FeZn	67·0
FeTh	87·3	FeCa	64·0
FeK	83·0		

It will be at once evident that "oxygen carriers" appear to be the *sine qua non* for ammonia oxidation, and the enhanced activity of binary and ternary mixtures of the oxides of those elements which possess at least two or more well-defined oxides indicates some relationship in this case between the catalytic activity and the presence of an oscillating higher and lower oxide functioning as an oxygen carrier. The presence of a number of oxides evidently increases the temperature range of catalytic activity by affecting the stability of the oxides.

It is interesting to note that chromium oxide ex chromium salts is practically inert, but the oxide obtained by the ignition of ammonium bichromate exerts a very marked catalytic activity.

The observation of Ostwald and Brauer, namely, that the period of contact with non-platinum catalysts must considerably exceed that necessary for platinum, has been repeatedly confirmed. The practical difficulties associated with the uniform heating, and at the same time ensuring a uniform stream-line flow through a shallow bed of small briquettes or powders of such materials, also presents grave technical disadvantages. These, however, seem to have been overcome in certain German factories.

The Oxidation of Hydrochloric Acid

For the manufacture of bleaching powder, by the absorption of chlorine gas in slaked lime, large quantities of chlorine are annually consumed, and consequently the economical production of chlorine becomes one of the serious problems confronting the alkali industry in its course of development.

In 1823 the Leblanc soda process was introduced into England by Muspratt. At first the hydrochloric acid resulting from the salt-cake process was turned into the air, but, owing to the pressure of the Alkali Acts of 1863 and 1874, as well as the serious competition of the Solvay ammonia-soda process introduced in 1866, the utilisation of hydrochloric acid in the most profitable manner became necessary to ensure the financial stability of the older Leblanc process. With the increasing extension of electrolytic methods for the production of soda from salt and the displacement of bleaching powder by liquid chlorine in the industries, it appears possible that the final development of these processes has now been reached.

The Deacon process.—The possibilities inherent in the oxidation of hydrochloric acid by means of atmospheric oxygen attracted the attention of inventors at a very early date, notably Oxland in 1840, Vogel and Thibierge in 1855, and Binks in 1860 It was not, however, until 1868 that H Deacon and F Hurter established the process as a satisfactory technical industry.

In its earliest form the hydrochloric acid from the salt-cake pans

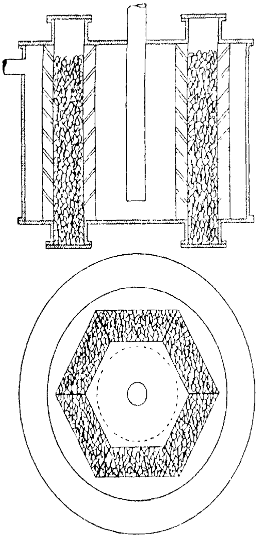

FIG. 11

was mixed with four volumes of air and passed through iron superheaters to the contact chambers The contact chambers or decomposing towers were iron cylinders about 12 feet wide filled with broken clay brick impregnated with cuprous chloride (Fig 11) (the brick containing from 0·6 to 0·7 per cent of copper as the chloride), maintained at 500° by the waste heat from the superheaters. About two-thirds of the hydrochloric acid was found to be oxidised according to the equation

$$4HCl + O_2 = 2H_2O + 2Cl_2.$$

Condensation of the steam and unchanged hydrochloric acid was effected in earthenware pipes, whilst the residual 5 per cent to 10 per cent of chlorine gas was dried in sulphuric acid prior to absorption in slaked lime.

Several technical difficulties were inherent in the earlier plants, notably the loss of most of the " pan acid " and all the " roaster acid " from the Leblanc process, the impossibility of obtaining a continuous supply of gas, the rapid poisoning of the catalyst, and the very indifferent yields obtained.

Hasenclever, in 1883, introduced the method of purifying the hydrochloric acid by absorption in water and blowing the purified gas out again by air in the presence of sulphuric acid. A sulphuric acid drier for the gases prior to passage through the superheater was simultaneously introduced. By this method a continuous supply of pure gases free from poisons such as sulphuric acid, $FeCl_2, SO_2, As_2O_3$, and carbon dioxide was thus obtained. The life of the catalyst was extended to from ten to twelve weeks, and more than 12 tons of bleaching powder could be prepared with the loss of only 1 ton of impregnated clay. Subsequent improvements in the yield were made as a result of the investigations of J. H. Harker,[1] Lunge and Marmier,[2] G. N. Lewis,[3] and Vogel v. Falckenstein.[4]

It was evident that the process involved the partition of hydrogen between oxygen and chlorine, the reaction

$$4HCl + O_2 \rightleftarrows 2Cl_2 + 2H_2O$$

being strictly reversible. Also the function of the cuprous chloride was shown to be purely catalytic in establishing the equilibrium at the temperature of operation.

The values of the equilibrium constant $K = \frac{C^2_{H_2O} \cdot C_{Cl_2}{}^2}{C^4_{HCl} \cdot C_{O_2}}$ at different temperatures were investigated, using the dynamic method by von Falckenstein, who passed different gas mixtures of the four constituents over cupric chloride and platinic chloride catalysts, maintained at suitable temperatures in an electric furnace. G. N. Lewis utilised the static method, obtaining equilibrium when commencing with mixtures of hydrochloric acid and oxygen.

The following results were obtained :

Temperature.	log K.
352°	2·43
356	1·90
419	1·52
450	1·40
600	0
650	−0·4

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[1] *Zeitsch. physikal. Chem.*, 1892, **9**, 673.

[2] *Zeitsch. angew. Chem.*, 1897, 108.

[3] *J. Amer. Chem. Soc.*, 1906, **28**, 1380.

[4] *Zeitsch. physikal. Chem.*, 1909, **65**, 371.

If the heat of reaction Q (13,800 cals.) be assumed to be independent of the temperature, Lewis showed that the values of K at various temperatures could be calculated from the following equation

$$\log_{10} K = \frac{6036}{T} - 7.241$$

The reaction may of course be considered as the combination of two simpler reactions

$$2H_2O \rightleftarrows 2H_2 + O_2,$$
$$2HCl \rightleftarrows H_2 + Cl_2,$$

if $$K_1 = \frac{p^2_{H_2} \cdot p_{O_2}}{p^2_{H_2O}} \text{ and } K_2 = \frac{p_{H_2} \cdot p_{Cl_2}}{p^2_{HCl}}$$

then $$\log_{10} K = 2 \log_{10} K_2 - \log_{10} K_1$$

Adopting Nernst and Wartenberg's figures for the dissociation of water vapour at high temperatures

$$\log_{10} K_1 = -\frac{25050}{T} + 1.75 \log_{10} T + 0.00028\ T - 0.2,$$

and employing for K_2 the value from the corresponding investigations of Dolezalek and Lowenstein on the dissociation of hydrochloric acid

$$\log_{10} K_2 = -\frac{9626}{T} + 0.8,$$

it follows that

$$\log_{10} K = \frac{5790}{T} - 1.75 \log T - 0.00028\ T - 1.4$$

Either of the above equations gives values of K which approximate very closely to the observed values. Nernst[1] gives the following calculated values, in close agreement with the determinations of v. Falckenstein

Temperature	log K
450	1.50
600	0.009
650	0.430

The fractional conversion of hydrochloric acid in dry air into chlorine can be calculated in a similar manner to that detailed in the oxidation of sulphur dioxide by the contact process. If x be the percentage of the hydrochloric acid, it is easily seen that

$$\sqrt[4]{K} = \frac{C^{\frac{1}{2}}_{H_2O} \cdot C^{\frac{1}{2}}_{Cl_2}}{C_{HCl} \cdot C^{\frac{1}{4}}_{O_2}} = \frac{x}{2(1-x)C^{\frac{1}{4}}_{O_2}}$$

Excess of oxygen is thus beneficial to the yield of chlorine, but the conversion is not appreciably affected by slight alterations in the air supply owing to the dependence of the equilibrium on the fourth root of the oxygen pressure only.

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[1] *Application of Thermodynamics to Chemistry*, 89

The increase in the values of K with decrease in temperature pointed to the necessity of finding suitable catalytic material for increasing the reaction velocity at low temperatures. No catalyst has as yet been found superior or even equal to Hurter and Deacon's cuprous chloride. With pumice impregnated with cuprous chloride Lunge and Marmier found that catalysis was already commencing at 310°, but the reaction velocity was still very slow below 400°. At 450°-460° the reaction velocity is sufficiently rapid to give a satisfactory yield under technical working conditions.

Hurter suggested the use of cuprous chloride from a survey of the heats of formation of the chlorides and oxides of the various elements, showing that no other element except copper formed oxides and chlorides in which the combination was of so loose a character[1] The mechanism of the reaction according to Deacon is based on the following cycle

$$2CuCl_2 = Cu_2Cl_2 + Cl_2,$$
$$Cu_2Cl_2 + O = CuO . CuCl_2,$$
$$Cu_2Cl_2O + 2HCl = 2CuCl_2 + H_2O$$

Levi and Bettoni, as the result of a series of experiments with various catalysts,[2] such as $CuCl_2$, $CuSO_4$, $MnCl_2$, $MgCl_2$, and hot pumice, arrived at the conclusion that the extraction of water was the chief function of the catalyst, and that temporary hydrate formation played an important role in the process :

$$CuSO_4 + 2HCl + O_2 = CuSO_4.H_2O + Cl_2,$$
$$CuSO_4.H_2O = CuSO_4 + H_2O$$

Subsequently the oxychloride, $CuO . CuCl_2$, was isolated and the original views of Deacon and Hurter received further support in the discovery that most substances capable of forming oxychlorides were catalytically active. There is some evidence, however, that the whole of the catalyst is not converted to the oxychloride at any stage in the process, suggesting that the oxide ion enters here and there into the lattice of the cuprous chloride, and is then again replaced.

V. Falckenstein drew attention to the necessity of carefully drying the gases before catalysis, and he showed that if the effluent gases were dried by sulphuric acid and again passed through the catalyst the conversion would rise from 82·5 to 85 per cent, and on a further passage to 88 per cent, owing to the shifting of the equilibrium ratio, $\frac{HCl}{Cl_2}$, by the abstraction of the water formed during the reaction.

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[1] *J. Soc. Chem. Ind.*, 1883, **2**, 106.

[2] *Gazzetta*. 1905, **351**, 320.

The two technical difficulties associated with the use of cuprous chloride as a catalyst are its sensitiveness to poisons and its volatility at the lowest working temperature, 450°

Hasenclever's method of purification of the hydrochloric acid effects a very considerable improvement in the purity of the gas, but sulphur dioxide, as well as sulphuric acid spray, are not entirely eliminated. Kolb, in 1891, suggested the further purification by passage over hot salt maintained at 450°, whereby sodium sulphate was formed, and a small additional quantity of hydrochloric acid would pass on with the main gas stream

Less volatile but more inefficient catalysts than cuprous chloride have been proposed from time to time, but owing to the bad yields resulting from the higher temperatures employed they have not found technical application

Amongst the more important may be mentioned ferric chloride, suggested by Thibierge in 1855, and platinised asbestos, by Weldon, 1871 Hargreaves and Robinson (1872) suggested chromic oxide, De Wilde and Reychler mixtures of manganese and magnesium chlorides, in which a complex oxide was assumed to be an intermediary in the cycle of reactions :

$$3MgCl_2 + 3MnCl_2 + 4O_2 = Mn_3Mg_3O_8 + 6Cl_2,$$
$$Mn_3Mg_3O_8 + 16HCl = 3MgCl_2 + 3MnCl_2 + 8H_2O + 2Cl_2$$

Ditz and Margosches, in 1904, employed the chlorides of the rare earths, whilst Dieffenbach, in 1908, suggested the double chlorides of copper and other elements

Mond[1] put forward a somewhat ingenious scheme to obtain more concentrated chlorine gas than that obtained in the usual Deacon process. If air and hydrochloric acid be passed alternately over heated nickel oxide deposited on pumice, the oxidation of the hydrochloric acid can be made a two-stage process through the intermediary formation of nickel chloride, which is reconverted into the oxide by the air The idea does not seem to have been developed

The Weldon process. – In 1869 W Weldon[2] introduced, at St Helens, a process for the oxidation of hydrochloric acid in solution At one time the process had a very considerable industrial importance, but is now being supplanted by modifications of the Deacon process already described.

Weldon's process suffers from the disadvantage that nearly 60 per cent of the original hydrochloric acid is lost in the form of calcium chloride, in addition to 3 per cent by weight, on the chlorine obtained, of the catalyst, manganese dioxide (pyrolusite); but its development was doubtless due to the great advantage it possessed over the Deacon process, in that the chlorine gas evolved was very concentrated The method of technical operation is as follows: hydrochloric acid, approximately 30 per cent strength, is first oxidised by means of manganese dioxide:

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[1] B P. 17272/1889

[2] B P 8308/1886

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

The spent manganese chloride solution is then carefully neutralised with limestone, and after removal of any ferric hydroxide by precipitation, is made alkaline by the addition of milk of lime, 30 per cent in excess of that required to precipitate all the manganous hydroxide being added:

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2.$$

The Weldon "mud" is now aerated at 50°-60° for several hours, calcium manganate being finally precipitated:

$$2Mn(OH)_2 + O_2 + Ca(OH)_2 = CaO \,.\, 2MnO_2 + 3H_2O.$$

On the addition of more manganous chloride and lime during the process of aeration, a further oxidation ensues:

$$2CaO \,.\, MnO_2 + 2Ca(OH)_2 + 2MnCl_2 + O_2$$
$$= 2(CaO \,.\, 2MnO_2) + 2CaCl_2 + 2H_2O.$$

It will be noted that when the regenerated manganese dioxide is used for the oxidation of a fresh quantity of hydrochloric acid a very considerable quantity of free base has first to be neutralised, thus again lowering the conversion efficiency of the process.

The mechanism of the process depends essentially on the use of the manganese salt as an oxygen carrier. Although we can show from the previous considerations in the Deacon process that atmospheric oxygen should be able to displace the chlorine from even weak solutions of hydrochloric acid, no active catalyst for this reaction has yet been found. If we extrapolate from v. Falckenstein's figures, the probable value of $K = \frac{[H_2O][Cl_2]}{[HCl]^2[O_2]^{1/2}}$ at 0°, we obtain a value of $K = 10^7$. The solubility of chlorine gas under 1 atmosphere is about 1 grm per litre, and of oxygen under two-fifths of an atmosphere 0·007 grm per litre, or $\frac{[Cl_2]}{[O_2]^{1/2}}$ in a liquid saturated with both gases at the respective pressures $= \frac{1}{0{\cdot}085}$ approximately. Hence $\frac{[H_2O]}{[HCl]^2} = 10^7 \times 0{\cdot}085 = Ca10^6$. That is to say, the dilution below which atmospheric oxygen would be inoperative in displacing chlorine from hydrochloric acid is remarkably small.

Weldon relied upon the preparation of a more active oxidising agent than atmospheric oxygen, so that the oxidation of the acid might proceed at reasonable velocities. The method by which the oxidising power or oxidising potential of atmospheric oxygen is raised above its normal value at the expense of the energy lost in the combination of the acid with the free alkali, is an interesting one.

We may write the oxidation reaction as follows:

$$\mathrm{MnO_2 + 2H_2O} \rightleftarrows \mathrm{Mn(OH)_2 + 2(OH)' + 2\oplus} \rightleftarrows$$
$$\mathrm{Mn^{\cdot\cdot} + 2(OH)' + 2(OH)' + 2\oplus}$$

The potential difference between an $(\mathrm{MnO_2})$ electrode immersed in the Weldon mud and the solution itself is given by the equation

$$E = E_0 + \frac{RT}{2\epsilon}\log\frac{[\mathrm{MnO_2}][\mathrm{H_2O}]^2}{[\mathrm{Mn^{\cdot\cdot}}][\mathrm{OH'}]^4} = E'_0 + \frac{RT}{2\epsilon}\log K\frac{\mathrm{H^{\cdot 4}}}{\mathrm{Mn^{\cdot\cdot}}},$$

since $[\mathrm{MnO_2}]$ and $[\mathrm{H_2O}]$ can be assumed to be constant.

If this electrode be coupled up with an auxiliary oxygen electrode in a neutral solution, neglecting the P.D. at the boundary of the Weldon mud and the electrolyte surrounding the oxygen electrode, the E.M.F. of the cell thus set up is obtainable from the following relationship:

$$\mathrm{PtO_2}\ \underset{\displaystyle E_1}{\Big|}\ \mathrm{Mn(OH)_2}\ \underset{\displaystyle E_2}{\Big|}\ \mathrm{MnO_2Pt}$$

$$V = E_1 - E_2 = E_0 + \frac{RT}{2\epsilon}\log\frac{C_0}{\sqrt{p_{O_2}}} - E'_0 - \frac{RT}{2\epsilon}\log\frac{\mathrm{H^{\cdot 4}}}{\mathrm{Mn^{\cdot\cdot}}}$$

The value of E_0 is approximately 1.22 volts, taking p as 1 atmosphere and a neutral electrolyte.

The value for E'_0 can be obtained from the investigations of Tower,[1] Inglis,[2] and Haehnel,[3] and may be taken as equal to the value $E'_0 = 1.35$ volts.

Hence

$$E_1 - E_2 = 1.22 - 1.35 + \frac{RT}{2\epsilon}\left(\log \mathrm{H^{\cdot 2}} - \log\frac{\mathrm{H^{\cdot 4}}}{\mathrm{Mn^{\cdot\cdot}}}\right)$$
$$= -0.13 + \frac{RT}{2\epsilon}\log\frac{\mathrm{Mn^{\cdot\cdot}}}{\mathrm{H^{\cdot 2}}} = -0.13 + \frac{RT}{2\epsilon}\log \mathrm{Mn^{\cdot\cdot}(OH')^2}\frac{1}{c^2},$$

where c is the value of the product $C_H C_{OH} = C_H^2$ in pure water.

In a neutral solution the solubility coefficient $\mathrm{Mn^{\cdot\cdot}(OH')^2} = 4\times 10^{-14}$ approximately.

Hence

$$E_1 - E_2 = -0.13 + 0.029\log\frac{4\times 10^{-14}}{(0.5\times 10^{-14})^2} = -0.13 + 0.45 = 0.32 \text{ volt}$$

In a similar manner we can calculate the P.D. of the cell in normal hydrion concentration and with a normal $\mathrm{Mn^{\cdot\cdot}}$ concentration:

$$V = -0.13 + \frac{RT}{2\epsilon}\log \mathrm{Mn^{\cdot\cdot}} - \frac{RT}{2\epsilon}\times 2\log \mathrm{H^{\cdot}} = -0.13$$

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[1] *Zeitsch. physikal. Chem.*, 1895, **18**, 17, 18.

[2] *Zeitsch. Elektrochem.*, 1903, **99**, 226.

[3] *Ibid.*, 1909, **15**, 834.

For a normal $Mn^{\cdot\cdot\cdot\cdot}$ concentration the P.D. would obviously be much greater.

Thus in acid solutions the oxidising potential of the MnO_2 electrode exceeds that of atmospheric oxygen and necessarily that of chlorine, since in *n*-hydrion concentration the cell, PtO_2 Cl_2 Pt, has an E.M.F.

$$V_1 = V_0 + \frac{RT}{2\epsilon} \log \frac{p_{O}{}'' p_{Cl}}{\sqrt{p_{O_2}}(p_{Cl})^2} = 1{\cdot}493 - 1{\cdot}35 = 0{\cdot}14 \text{ volt},$$

indicating that the manganese " mud " has an oxidising potential at least 0·27 volt higher than the liberated chlorine, thus giving a measure of the energy available for oxidation of the hydrochloric acid. In neutral solutions the manganese " mud " possesses an oxidising potential inferior to that of oxygen or of chlorine.

In actual practice more alkali has to be added than is necessary to ensure the oxidation of the manganous salt. In the early experiments of Weldon, red solutions were occasionally obtained during the process of oxidation, and it was found that the quantity of manganese dioxide formed during aeration was very small. It was finally shown that the red colour was due to the formation of manganous manganic oxide, owing to a deficiency of base, according to the interaction

$$MnO_2 + \tfrac{1}{2}H_2O \rightleftarrows \tfrac{1}{2}Mn_2O_3 + OH' + \cdot\,,$$

where
$$E = E_0 + \frac{RT}{\epsilon} \log \frac{(MnO_2)(H_2O)^{\frac{1}{2}}}{(Mn_2O_3)^{\frac{1}{2}}(OH')}$$

or
$$E = E_0 + \frac{RT}{\epsilon} \log C \frac{H^{\cdot}}{Mn^{\cdot\cdot\cdot\cdot}}.$$

Other processes for the oxidation of hydrochloric acid. Owing to the inefficiency of the Weldon process from the yield point of view, the inventor and Péchiney experimented for many years on the production of chlorine by the aid of the following cyclic process

$$4MgCl_2 + 2H_2O + O_2 = 4MgO + 4HCl + 2Cl_2,$$
$$MgO + 2HCl = MgCl_2 + H_2O$$

A pure magnesium chloride was not utilised, but the crude liquor after evaporation was mixed with the required amount of powdered magnesia to form the oxychloride, $MgO \cdot MgCl_2$, prior to drying at 300°. The chlorine and hydrochloric acid together with some steam were removed by an air blast at 1000°.

Another ingenious process which has been the subject-matter of various patents involves the following cyclic process, in which oxides of nitrogen play the part of catalysts, as in the sulphuric-acid lead-chamber process :

$$3HCl + HNO_3 = Cl_2 + NOCl + 2H_2O,$$
$$HNO_3 + NOCl = N_2O_4 + HCl.$$
$$N_2O_4 + 2HCl = N_2O_3 + H_2O + Cl_2,$$
$$N_2O_3 + O_2 + H_2O = 2HNO_3.$$

This idea, developed by Dunlop in 1849, together with the Weldon Péchiney process outlined above, does not appear to have received any considerable technical development

THE FRACTIONAL COMBUSTION OF HYDROGEN SULPHIDE

We have already indicated the technical significance of the catalytic processes employed for the oxidation of sulphur dioxide to sulphuric anhydride A great part of the dioxide utilised for this purpose is derived from the combustion of natural sulphides, especially pyrites and blende, or from artificial sulphides such as gas-works spent oxide yet a certain quantity is always obtained from the combustion of elementary sulphur. In 1882 Claus introduced a method for the fractional combustion of hydrogen sulphide into sulphur and water, thus preparing sulphuric acid by a three-stage process

$$(1)\qquad 2H_2S + O_2 = 2H_2O + 2S,$$
$$(2)\qquad 2S + 2O_2 = 2SO_2,$$
$$(3)\qquad 2SO_2 + O_2 + H_2O = H_2SO_4$$

It has been suggested that the combustion of hydrogen sulphide to sulphur dioxide could be accomplished in one stage, which, in the presence of excess of air, could be used directly for the preparation of sulphuric acid This idea does not seem to have received any technical development, chiefly on account of the very large quantities of diluent nitrogen present in the resulting sulphur-dioxide gas mixture

The Claus process, however, in the hands of A M Chance, has been developed, and at the present time is the most satisfactory method of dealing with the alkali waste of the Leblanc soda process

Alkali waste contains some 40 per cent of calcium sulphide, 20 per cent of calcium carbonate, and 10 per cent of lime, the residue consisting chiefly of silicates with small quantities of sodium carbonate and iron sulphate Chance modified Gossage's (1838) process for the production of a gas rich in sulphuretted hydrogen by decomposition with carbon dioxide Carbon dioxide from lime-kilns is passed through a set of carbonating towers through which a suspension of alkali waste flows in the counter-current direction In the first tower sulphuretted hydrogen is evolved according to the equation

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S$$

The hydrogen sulphide diluted with the nitrogen in the original kiln gas passes to the second tower, in which the hydrogen sulphide is absorbed, with the formation of calcium hydrosulphide

$$CaS + H_2S = H_2CaS_2$$

On carbonating this solution a gas containing twice as much hydrogen sulphide as was obtained from the first tower is evolved and collected in gas-holders over water covered with a layer of oil

The sulphuretted hydrogen thus obtained, of about 38 per cent purity, is mixed with air in the proportion of 5 volumes of gas to 4 volumes of air and passed into the Claus kiln for fractional combustion into sulphur and water vapour.

The Claus kiln consists essentially of a fire-brick cylinder containing a grating on which the catalytic material, usually bog iron ore (hydrated ferric oxide ignited at a low temperature), is deposited. The combustion is started by throwing a little red-hot coal into the furnace and is maintained by the heat of the reaction itself. The temperature of the eflowing gases, one foot from the kiln, should not exceed 300°, otherwise a loss of sulphur occurs. The hot gases are subsequently passed into a series of condensing chambers, where part of the sulphur condenses to the liquid state, and the rest is recovered as flowers of sulphur in the condensed steam.

In order to minimise the loss of sulphur compounds (H_2S or SO_2) in the effluent gases, the exact theoretical ratio, $H_2S : O_2$, required for combustion in the entering gases must be maintained The temperature of the catalyst is mainly determined by the speed of passage of the gas.[1]

Various other catalytic materials for this combustion process have been utilised, such as broken fire-brick, bauxite, and dried Weldon mud. There are, however, two distinct advantages in making use of an active catalyst which will operate at low temperatures First, the life of the kiln and the condensing chambers is considerably shortened by high temperature operation, and, secondly, above 200° an interesting reverse reaction between the sulphur and the steam formed begins to take place with appreciable velocity.

$$2H_2O + 3S \rightleftarrows 2H_2S + SO_2.$$

It is extremely probable that the flowers of sulphur recovered in the condensed water do not originate in the original condensate of sulphur vapour from the combustion process, but result from the interaction in solution of the sulphur dioxide and hydrogen sulphide formed in the lower parts of the kiln and in those condensers which are above 100° to 200°.

The catalytic activity of oxides of iron and manganese in the Claus process is usually attributed to the property these elements have of forming more than one oxide, thus permitting the assumption of an oscillating oxide acting as oxygen carrier:

$$\begin{tikzcd}
Fe_2O_3 \arrow[d] & O_2 \arrow[l] \arrow[r] & O_3Fe_2 \arrow[d] \\
H_2S \arrow[r] & Fe_2O_2 \arrow[u] & H_2S. \arrow[l]
\end{tikzcd}$$

Some experiments by the writers, however, indicate that iron sulphide is an intermediary compound in the process of oxidation, and that the mechanism of oxidation can be more truly represented on the following lines, making the Claus process simply an extension of the ordinary gas-works process of spent oxide revivification.

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[1] See, however, Carpenter and Linder, *J. Soc. Chem. Ind.*, 1903, **22**, 457; 1904, **23**, 557.

$$Fe_2O_3 + 3H_2S \rightleftarrows 2FeS + 3H_2O + S,$$
$$4FeS + 3O_2 \rightleftarrows 2Fe_2O_3 + 4S$$

CATALYSIS IN THE PURIFICATION OF ILLUMINATING GAS AND GASEOUS FUELS

As is well known, illuminating gas after leaving the scrubbers contains various quantities of substances which are deleterious in the uses to which the gas is subsequently put. Thus, in addition to substances like carbon dioxide, which lower the illuminating power and calorific value of the product, the scrubbed gas may contain anything from 0.5 to 2.0 per cent of sulphuretted hydrogen as well as organically combined sulphur compounds, such as carbon disulphide, thiophene, and mercaptans, to the extent of 10 to 80 grains of sulphur per 100 cubic feet of gas. Such sulphur compounds, since, on combustion, they yield sulphur dioxide, are disagreeable constituents of the final product. Their removal is consequently desirable. Indeed the removal of free sulphuretted hydrogen is required by statutory regulation. Formerly, also, the removal of the combined sulphur to a certain degree was also required by statute, but this is no longer required.

In practice it is the custom to free illuminating and other gases from sulphuretted hydrogen by passing them through various suitably moistened absorbent materials, among which the more commonly employed are lime, oxide of iron, and manganese dioxide in the form of Weldon mud. The former removes both carbon dioxide and the sulphuretted hydrogen, together with a fraction of the carbon disulphide present. Its use, however, is becoming more and more restricted, especially to small undertakings having a local market for the product, since the disposal of the spent lime, containing both carbonate and a sludge of calcium sulphide, is both difficult and disagreeable owing to the obnoxious odour which the material possesses. The oxides of iron and manganese are increasingly used, and in a manner which involves their functioning as catalysts.

The elimination of sulphuretted hydrogen by means of oxide of iron is carried out in huge boxes carrying the absorbent material. This is generally employed in the form of bog iron ore, which, from its content of organic matter, is porous and thus favours ready transformation to sulphide. If the precipitated hydroxide be employed, the material is generally lightened by admixture with organic matter in the form of sawdust. The material is at all times kept suitably moist. Absorption of the sulphuretted hydrogen involves a change of the absorbent from the brownish hydrated oxide to the blackish-green sulphide. Ferric sulphide and ferrous sulphide and sulphur are the products of the transformation, which may be symbolised by the equations

$$Fe_2O_3 + H_2O + 3H_2S = Fe_2S_3 + 4H_2O,$$
$$Fe_2O_3 + H_2O + 3H_2S = 2FeS + 4H_2O.$$

After absorption ceases, the sulphides, by exposure to air, may be transformed into the original material with the simultaneous production of sulphur, which change may be represented by the equations

$$2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 6S,$$
$$4FeS + 3O_2 = 2Fe_2O_3 + 4S.$$

Thus, by alternation of the process of absorption and of exposure to air, or revivification, the original oxide of iron may effect the catalytic conversion of the sulphuretted hydrogen to sulphur and thereby the removal of the sulphur from the gas As much as 50 per cent of sulphur may thus be accumulated in the oxide by alternation of the two stages, and the resultant material is then a convenient source of sulphur for sulphuric acid manufacture.

In actual operation under working conditions, illuminating gas generally contains small amounts of oxygen entering the gas through leakages in the system. This oxygen effects, to a certain degree, in the boxes, the process of revivification attained otherwise by exposure to air. The observation of this action of oxygen has led to a development of modern gas purification in which the oxygen content of the gas at the entrance to the oxide purification system is controlled, and, if necessary, air is added to the gas to be purified to facilitate the process of revivification *in situ* Thus, the process of purification becomes in essence the catalytic conversion, by means of oxide of iron acting as catalyst, of sulphuretted hydrogen and oxygen to sulphur and water, according to the equation

$$2H_2S + O_2 = 2H_2O + 2S + 110{,}000 \text{ cals}$$

The advantage to be obtained from the admission of air to the purification system is that the purifiers can be worked for much longer periods without recharging. In modern gas-works practice this period may amount to as much as six months per box with a system of purification employing four boxes in series The amount of oxygen added is restricted by two factors, the diluent effect on the gas of the nitrogen simultaneously added and the fact that the heat effect of the reaction may be so great locally as to cause combustion of the material in the purifiers, with consequent introduction of sulphur dioxide into the gas and disorganisation of the purification system. The care requisite in this regard will readily be appreciated by the gas engineer who has knowledge of the strongly exothermic nature of the reaction, which, as given in the equation above, amounts to 110,000 cals.

Precipitated oxide of iron, an artificially prepared material, has come into considerable use as the catalytic material, since its action is found to be more vigorous than the natural bog iron ore. For similar reasons, the manganese dioxide of Weldon mud is also employed, its reactivity with sulphuretted hydrogen being computed to be five times that of the bog ore. All the materials are employed until so far loaded with sulphur that they are available as an economical source of sulphur.

It is to be pointed out that all the fuel gases of industry contain greater or less amounts of sulphuretted hydrogen, and are therefore potential sources of sulphur supply for the sulphuric acid industry. The gases from by-product coking ovens are also a further such source. Since, however, the capital outlay in plant and space for oxide box purification is considerable, the economy of the purification process is small, and these sources of sulphur have to a marked degree been neglected, the sulphur being left in the gas with consequent vitiation of the atmosphere in the neighbourhood of their combustion. It is to be hoped that further improvement may be effected in the recovery of sulphuretted hydrogen from all fuel gases, so as to render its removal a sound economic proposition and thereby minimise the dependence of the community for sulphur upon foreign sources of supply.

The elimination of sulphuretted hydrogen from coal gas by the methods just outlined is remarkably complete, and with skilled supervision the quantities of such gas in modern illuminating gas are negligible. The process, however, except when lime is employed, fails to bring about the removal of the organically combined sulphur compounds, and, in the case of lime, only partial removal of carbon disulphide is effected. Attempts to eliminate organically combined sulphur are almost as old as the illuminating gas industry itself, and as many of the suggested processes are catalytic in nature their record is essential here.[1] So far back as 1806 Edward Heard suggested passing the crude gas over alkaline earth or certain metals or their oxides placed in iron tubes or other vessels and exposed to a furnace. In 1818 Palmer took out patents upon a process of removal by passage of the crude coal gas through heated tubes containing iron, oxide of iron, or iron stone, so disposed as to present as large a surface as possible. In the 'fifties Thompson suggested a process to operate upon a technical scale, of which the principle is merely to pass the gas over lime heated to a dull red or much lower, or small pieces of brick or pumice-stone previously steeped in a solution of the chloride of platinum. Bowditch, in 1860, patented a process for removal of combined sulphur by passing the gas first freed from sulphuretted hydrogen in the ordinary manner through heated clay, oxide of iron, or lime, the temperature found most efficient being between 140° and 215°. In 1870 Vernon Harcourt proposed to decompose organic sulphur compounds by placing a mass of iron turnings or wire into the mouthpiece of each retort or by conducting the gas through heated tubes partially filled with suitable surface-presenting material, and a trial was made in 1874 of the process suitably modified for technical operation. I. von Quaglio, in 1878, proposed the use of heated clay balls impregnated with the chloride of a metallic catalyst, or such metals themselves in powdered form.

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[1] Carpenter, *Purification of Gas by Heat*.

All these processes are in reality suggestions for conducting readily by means of catalytic agents a reaction which may be illustrated best with reference to carbon disulphide by means of the equation

$$CS_2 + 2H_2 = 2H_2S + C$$

Upon the laboratory scale this is readily effected and forms the basis of the Harcourt test for such sulphur compounds. As actually operated in the test, the gas is passed through a heated flask containing platinised pumice. The disulphide is decomposed quantitatively, and the formation of sulphuretted hydrogen determined by means of a colour test.

The installation of such a process of purification upon a large technical scale for the purification of illuminating gas is due to Hall and Papst, of the Portland Gas and Coke Co., Oregon, U.S.A. The device patented by Hall for the purpose is composed of two heaters filled with chequer-work as in a water-gas plant, and a generator from which they are heated internally and alternately by producer gas. Whilst the coal gas is being treated for sulphur compounds in the one heater, the other is being heated up by the gas from the generator, and so continuity of purification is ensured. During 1909 as many as 817 million cubic feet of gas were heated in this way at an average cost stated to be ½d per 1000 cubic feet. The percentage reduction of combined sulphur in the gas throughout the year averaged 70 per cent, reducing the content from an average of 59 grains to 17 grains per 100 cubic feet. The temperatures employed were high (up to 900° is suggested), so that doubtless there would be an accompanying loss in illuminating power. The percentage reduction increased with increasing temperature, varying from 20 per cent at 127° to 76 per cent at 704°.

The work of Carpenter and Evans[1] in England upon similar lines may now be detailed. A variety of catalytic materials for the decomposition of the organic sulphur by means of hydrogen were studied with a view to their application upon a practicable scale. Among such materials may be mentioned fire-brick, pumice, iron oxide, platinum, and nickel. Of the contact materials studied, pumice or fire-clay impregnated with finely divided nickel was chosen as the most suitable, being the most active and not prohibitive in cost. After smaller scale experiments, a large-scale plant with a capacity of 1¾ million cubic feet per day was erected. This was later supplemented by a plant dealing with 10 million cubic feet per day in London and one at East Greenwich in five units, each unit capable of dealing with 3 million cubic feet of gas per day The gas to be heated is previously freed from sulphuretted hydrogen in the usual way and passes through a system of preheaters and heat interchangers to the reaction chamber, maintained at 450°, at which temperature approximately 80 per cent *conversion of the sulphur compounds may be obtained The heated gas leaving the reaction chamber flows through the heat exchangers* in the contrary direction, and permits therefore of economy in the heat required to be added to the system In the East Greenwich plant the weight of metallic nickel employed is 1321 lbs, equivalent approximately to 1 lb of metallic nickel per 10,000 cubic feet of gas per day The daily consumption of coke for the same plant amounts to 5½ tons per day. Provision is made for regeneration of the catalytic material after a period of use. This is necessary owing to the deposition of carbon resulting from the reaction in the catalytic material employed Regeneration is effected by blowing hot air through the system, which burns off the carbon deposit from the fire-clay ball impregnated with nickel The average reduction of sulphur content in the 10 million cubic feet per day plant over a period of sixteen months was from 40 to 8 grains per 100 cubic feet, or a percentage reduction amounting to 80 per cent The effective reduction is to a certain degree governed by the sulphur content of the gas, a maximum reduction, equivalent to 84 per cent, being observed on a gas of 61 grains of sulphur per 100 cubic feet, the minimum being 72 per cent on a gas of 19 grains sulphur content The effect of the process on the illuminating power of a rich 20-candle-power gas was specially studied It was found that the illuminating power was unimpaired, the average quality before and after treatment for sulphur being 20·54 and 20·46 candles respectively The cost of working the sulphur extraction process is given as 0·3d per 1000 cubic feet, including fuel maintenance charges depreciation, and interest The capital cost works out at £1500 per million cubic feet of gas per day

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[1] Carpenter, *J. Gas Lighting*, 1914, **126**, 928; Evans, *J. Soc. Chem. Ind.*, 1915, **34**, 9.

It is possible that yet another catalytic reaction may be employed technically, in the future, for removal of the combined sulphur from fuel and illuminating gases It is well known that carbon disulphide reacts at suitable temperatures with water to form carbon dioxide and hydrogen sulphide, according to the equation

$$CS_2 + 2H_2O = CO_2 + 2H_2S$$

In a French process patented by Guillet[1] this reaction is accelerated catalytically by means of oxide of iron maintained at temperatures between 80° and 300° Reduction on a laboratory scale from 16 to 4·3 grains per 100 cubic feet was claimed at 130°

The sulphuretted hydrogen formed is fixed, however, by the iron oxide, and hence the process, conducted in the above manner, must necessarily be discontinuous. On the other hand, it is known, for example, that in the catalytic hydrogen process employing water gas and steam at 500° with iron oxide as basic catalytic material, all sulphur compounds are converted to hydrogen sulphide in the course of the reaction and pass on as such with the other products. It does not seem unlikely, therefore, that such a catalytic process for sulphide removal could be operated continuously if the right conditions were obtained. The reaction would possess a point of advantage over the processes previously considered, since carbon dioxide, and not carbon, is the product of conversion. The catalytic mass, therefore, would remain unaltered and the process of aeration requisite in the Hall and Papst and in the Evans-Carpenter processes would be unnecessary. Interesting technical developments of the process of M. Guillet may therefore be expected.

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[1] *Soc Tech, de l'Ind du Gaz en France*, 1912, p 245

THE INFLUENCE OF CATALYSTS IN SURFACE COMBUSTION

During recent years a considerable advance has been made in the technical application of the catalytic process of surface combustion by Schnabel in Germany, but more especially by Bone and his co-workers in England.[1]

In the preceding pages we have already discussed the catalytic activity of certain substances, notably platinum, in promoting the combination of oxygen and hydrogen as well as other combustible gaseous mixtures, and have noted that under suitable conditions the catalytic material can attain quite high temperatures. Thus Fletcher[2] appears to have been the first to study the conditions necessary to maintain the catalyst at a high temperature by the process of surface combustion. This investigator showed that it was possible by suitable regulation of the composition of a mixture of coal gas and air to keep a ball of iron wire continuously at a high temperature without any combustion taking place in the form of flame, provided that the gaseous mixture came in direct contact with the hot material.

Bone, in 1902, commenced a systematic investigation on the influence of various catalytic materials such as platinum, gold, silver, copper, and nickel oxides, and magnesia at fairly elevated temperatures, *circa* 500°.

He noted that there was a steady increase in catalytic activity with elevation of the temperature and that the disparity between different catalytic materials diminished with ascending temperatures.

As a logical sequence to these earlier experiments, the conditions necessary for maintaining a catalytic material continuously and uniformly at a high temperature by surface combustion were developed.

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[1] *Phil. Trans.*, 1906 (*A*), 206, *Ber*, 1913, **46**, 5, *Proc. Amer. Gas Inst*, 1912, **6**, 564; R.I. Lecture, Feb 1914.

[2] *J. Gas Lighting*, 1887, **1**, 168; see Bone, *loc. cit.*

Bone and M'Court's earliest types of apparatus consisted essentially of a porous fire-brick diaphragm through which a gas and air mixture in the correct ratio for complete combustion was forced by a suitable injector or blower. The fire-brick diaphragm rapidly attains a bright-red heat and complete combustion is effected in a very thin layer of the diaphragm (⅛ to ¼ inch). The advantages of such a heater, viz. the high efficiency in the production of effective radiant energy and the possibility of fixing the diaphragm in any position, are partly gainsaid by the necessity of using either air or gas under pressure, and by the fact that the diaphragms are slowly but continuously blocked up by dust and tar fog in the air or gas.

As a consequence the surface combustion heater was modified by substituting a bed of refractory granular material for a diaphragm and forcing through it a suitable mixture of air and gas or vaporised fuel. Many applications of this method have given extremely successful results in practice. Thus the granular material may be packed round muffles, crucibles or retorts or the flue tubes of steam boilers.

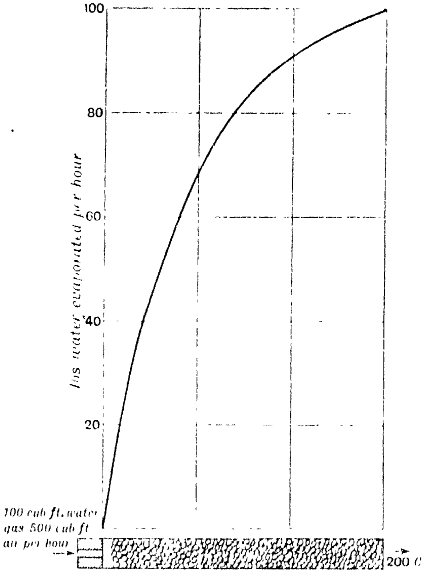
The following figures indicate the remarkable efficiency obtained when steam is raised by a gaseous fuel when this system of surface combustion is utilised.

Utilising a tube 3 feet long and 3 inches in internal diameter packed with granular refractory material as a heating unit, nearly 100 lbs of water could be evaporated per hour (20 to 22 lbs per square foot of heating surface) with 100 cubic feet of coal gas and 550 cubic feet of air, representing an 88 per cent transmission (to the water) of the net heat developed by the combustion (Fig. 12). This unit compared extremely favourably with the 50 per cent obtained with blast-furnace gas and the 65-70 per cent obtained with coke-oven gas when the usual gas firing systems are employed. It was noted that the effluent gas temperature was only 200°, and in later experiments even this small amount of heat originally lost was utilised to heat up the boiler feed-water. Even better results were obtained with a large boiler erected at the Skinningrove Iron Works. This boiler, fitted with 110 heating units of the above-mentioned size, was capable of evaporating 5000 lbs of water per hour with an average figure of 11.1 lbs per square foot of heating surface per hour, and on a ten-hour run gave the remarkably high figure of 92.7 per cent efficiency. The efficiency of this boiler may be judged by the following figures:

Heat utilised	92.7 per cent.
Heat lost in burnt gases	3.0 ,,
Heat lost by radiation	4.3 ,,
	100.0

Steam equivalent of power consumed by fan for driving the gases, 2·7 per cent. Net overall efficiency, 90·0 per cent.

More recent improvements in the "Bonecourt" boilers include a rigid system of refractory surfaces instead of a packing of granular material for dealing with gases liable to contain dust or tar fog, and an increase in the size of the heating unit. Experimental trials[1] have shown that heating units up to 6 inches in diameter and from 13 to 21 feet long can be constructed without affecting the high rate of evaporation per square foot of heating surface.



3 ft. unit heater for boiler, showing evaporation in lbs per foot

FIG. 12

THE INCANDESCENT MANTLE

The historical development of the incandescent gas mantle may be said to have commenced with the investigations of Drummond on the production of incandescent surfaces on certain refractories such as magnesia, lime, alumina, and zinc oxide by means of the oxy-hydrogen flame, whilst Berzelius first pointed out the uses of thoria and zirconia as light-emitting refractories From 1839 to 1880 several inventors were exercising their ingenuity in the production of light from the Bunsen burner flame, amongst whom may be mentioned Cruickshank in 1839, Tessié du Motay in 1867, and Edison in 1878 It was not, however, until the period 1881 83 that Williams, in New Jersey, and Auer von Welsbach, in Vienna, practically simultaneously developed what is essentially the gas mantle of to-day

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[1] Bone, *Coal and its Scientific Uses* (Longmans, 1918).

The earlier mantles were made of cotton and possessed grave defects, such as shrinkage with use, resulting in crumbling, a twist in the fibre, introduced in the spinning, making the mantle susceptible to shock, and, finally, a continuous diminution in light emissivity

Present-day mantles are generally made of artificial silk or grass cloth (ramie fibre) spun into threads

It may be noted in passing that all varieties of artificial silk appear suitable for the manufacture of mantle material, including the silk from Swann and Chardonnet's collodion process, the more recent Cross and Bevan viscose and acetate methods, and Schweitzer's cupro-ammonium solvent

Auer von Welsbach commenced his researches on the fractional crystallisation of the rarer elements in 1880, and during that year he noted that cotton threads could be impregnated so as to leave a coherent oxide ash as a skeleton The colour of the flame produced on heating this skeleton in a Bunsen burner varied from yellow to green In 1883 the earliest mantles were introduced in which the oxides of zirconium and lanthanum were chiefly used, although the addition of smaller quantities of other oxides was simultaneously suggested

In 1886 the use of thoria was patented,[1] and the idea of strengthening the finished mantle for transport by immersion in collodion was also claimed

None of these methods, however, proved satisfactory as far as life and light emissivity were concerned, these being the two most important factors for technical success From 1886 to 1891 Welsbach and his assistant Harbinger continued unsuccessfully their experiments upon the mantle, until an accidental observation that small quantities of ceria were always present in some specimens of thoria which possessed a somewhat higher emissivity than others led to the introduction of the present-day Welsbach mantle

The extraordinary effect that small quantities of ceria may exert on the emissivity of thoria is indicated in the accompanying curve (Fig 13) It will be noted that the maximum emissivity is obtained when a 99·1 per cent thoria–0 9 per cent ceria mixture is utilised[2]

Various theories have been put forward to explain the phenomenal increase in light emissivity in presence of ceria, but no satisfactory conclusion as to actual mechanism of light production has as yet been arrived at.

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[1] D R P 41945

[2] For a technical description of the manufacture of gas mantles, see R Bohm, *Die Fabrikation der Gluhkorper fur Gasgluhlicht*

Westphal's theory that during the period of optimum emissivity the gradual combination of an acid oxide, *e.g.* thoria, with a basic one such as ceria is taking place may be dismissed as untenable. Bunte's view is supported by a certain amount of experimental evidence. He regards the thoria as a heat-insulating surface and holds that the ceria catalytically hastens the combustion of the gas-air mixture; by this means the surface of the thoria is heated up to the temperature of the flame, viz. 1700° to 1870°, and radiates at this temperature. Rubens[1] has shown that a black body radiation temperature of at least 1600° would be necessary to produce a similar visible emissivity. It is, however, not clear why only 0·9 to 1 per cent of ceria exerts the maximum catalytic activity. Le Chatelier was of the opinion that thoria-ceria mixtures do not radiate as "Black body" radiators, but exert selective emissivity in the region of the visible rays. Bunte, however, has shown that the emissivities of ceria and thoria and the Welsbach mantle material when heated in a muffle to the same temperatures were not sensibly different.

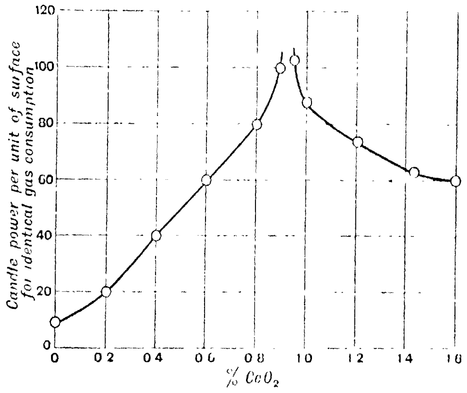

FIG. 13.

Wyrouboff and V. B. Lewis attributed the increased luminosity to the alternate oxidation and reduction of the ceria

$$O_2 + 2Ce_2O_3 \rightleftarrows 4CeO_2,$$

the presence of 1 per cent of ceria in the mixture being sufficient to ensure that combustion proceeds at its maximum velocity.

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[1] *Ann Physik*, 1906, **20**, 543.

An important observation was made by Meyer and Anschutz,[1] who noted that CeO_2 forms a solid solution in thoria up to 7 per cent and that a small quantity of CeO_3 was also present in a used mantle mixture. It is an interesting speculation as to whether the maximum dissociation of the cerium oxide in the thoria occurs in dilutions 0.9 to 1 per cent.

The loss of light emissivity with continued use is attributed by White and Muller[2] to the gradual volatilisation of the catalytic cerium oxide. Bruno,[3] on the other hand, considered that the cerium oxide became converted into an inert allotropic modification from which the active oxide could be regenerated by slowly cooling the mantle.

The investigations of Swan[4] on the catalytic effect of thoria-ceria mixtures on the combustion of electrolytic gas mixtures make it appear highly probable (see p. 103) that the ceria is in fact an oxygen-carrying promoter to the catalytic thoria.

As catalytic oxygen carriers chromium, vanadium, manganese, iron, cobalt, and even silver oxides have been suggested. With the exception of the three first-named, these oxides are much too volatile for practical use, unless retained on the mantle in the form of silicates, in which case their catalytic properties are considerably impaired. A composition of alumina and 8-16 parts of chromium oxide was largely used in the preparation of "Sunlight" mantles. With a thoria base, the following quantities of catalytic material are said to give roughly the same emissivity:

CeO_2, 0.9-1.0; V_2O_5, 0.4; MnO_2, 1.5; U_3O_8, 0.25 per cent.

Other bases, in addition to thoria and alumina, have been suggested from time to time, such as zirconia, magnesia, and lanthana-chalk mixtures. Magnesia has been shown to be rather volatile, whilst chalk suffers from the disadvantages of being readily attacked by water and carbon dioxide present in the air when the mantle is not in use.

Small quantities of the oxides of beryllium and aluminium are frequently added as hardeners in order to increase the resistant powers of the mantle.

THE PREPARATION OF FORMALDEHYDE

The earliest development of the formaldehyde industry was closely associated with its utilisation as a volatile disinfectant for rooms. For this purpose so-called formaldehyde lamps were introduced, in which methyl alcohol was caused to burn in specially constructed burners. A small fraction of the methyl alcohol was in this way converted into formaldehyde, but by far the greater portion was oxidised to carbon dioxide and steam, according to the equations

$$2CH_3.OH + O_2 = 2H.CHO + 2H_2O,$$
$$2CH_3.OH + 3O_2 = 2CO_2 + 4H_2O.$$

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[1] *Ber.*, 1907, **40**, 2639.

[2] *J. Gas Lighting*, 1903, **83**, 504.

[3] *Zeitsch. f. Beleucht.*, 1899, **5**, 244.

[4] *J. Chem. Soc.*, 1924, **125**, 780.

Modern room disinfection by means of formaldehyde is usually accomplished by the volatilisation of paraform $(H.CHO)_3$ (Schering's formalin) in small lamps, or by chemical oxidation of methyl alcohol, by the use of permanganate[1] or barium peroxide (bleaching powder has also been suggested, Eischengrun's Autan method).

The earlier alcohol combustion lamps devised by Tollens, Bartel, Robinson, Trillat, Broche, Dieudonné, and others are no longer in use.

As new industrial uses for formaldehyde were found, notably in the hardening of gelatins, preservation of food, disinfection of hides in certain leather-tanning processes, as well as in the recent development of synthetic tannins, phenol formaldehyde condensation products for electrical insulator and other purposes (baekelite), and the fine organic chemical industry, the most suitable method of production on a technical scale became a matter of importance.

At the present time it may be stated that the only technical processes for the preparation of formaldehyde are those based on the fractional combustion of methyl alcohol; but, as will be subsequently shown, these methods will probably be replaced by more economical catalytic processes which are still in the experimental state.

The earliest experimental work on the fractional combustion of methyl alcohol to formaldehyde dates from the time of Hofmann,[2] who obtained a small conversion by the passage of an air alcohol mixture through a red-hot platinum tube. Gartner, as well as Tollens and Loew,[3] effected certain modifications by substituting a glass tube packed with platinum or metallic copper foil as catalytic material; they laid stress on the influence of the presence of moisture in the original alcohol, the variability of yield with alteration in the oxygen alcohol ratio, and changes in the temperature of the catalyst. Trillat,[4] in 1889, first proposed a large-scale production plant in which crude methyl alcohol was evaporated, mixed with air, and passed through the catalyst chamber containing platinum asbestos maintained at a dull red heat. Other catalytic materials, such as copper oxide or even fire-brick, were suggested. As a result of a series of experiments, Trillat was able to oxidise methyl alcohol with air by means of an electrically heated platinum gauze at 200°; with elevation of the temperature, decomposition proceeds further, as shown by the increase in the carbon monoxide and dioxide content. The optimum steam content for the methyl-alcohol vapour was found to be in the neighbourhood of 20 per cent.

With oxidised copper gauze at 330°, Trillat obtained a 48·5 per cent yield with an air-alcohol ratio of 2·5 litres to 0·65 grm. In modern practice much higher temperatures are usually attained, *e.g.* 450°-550°.

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[1] Evans and Russell; see Croner, *Desinfecktion*, xi., 1909.

[2] *Ber.*, 1878, **11**, 1685.

[3] *Ibid.*, 1881, **14**, 2134; 1882, **15**, 1629, **20**, 141; cf. *J. pr. Chem.*, 1886 (ii.), **33**, 321.

[4] *Oxidation des alcohols*, 1901.

Later, Sabatier and Mailhe[1] directed attention to Berthelot's *experiments, in which he showed that the thermal decomposition of* primary alcohols in the absence of air was effected by two simultaneous reactions:

(*a*) A dehydration, *e.g.* $C_2H_5 \cdot OH \rightleftarrows CH_2{=}CH_2 + H_2O$,

(*b*) A dehydrogenation, $C_2H_5 \cdot OH \leftrightarrows CH_3 \cdot CHO + H_2$,

and proceeded to investigate the effect of various catalytic materials on these decompositions and showed that copper at a temperature of 200°-300° was an effective dehydrogenation catalyst.

With freshly reduced copper oxide, the reduction proceeds according to the equation

$$CH_3 \cdot OH \leftrightarrows H \cdot CHO + H_2,$$

and the reaction is a reversible one: a 50 per cent conversion is obtained with a 5 per cent loss of decomposition products and 45 per cent unchanged methyl alcohol, which can be fractionated off and returned to the alcohol storage reservoir.

Unfortunately, in the case of methyl alcohol, copper appears rapidly to lose its activity, either owing to the gradual reduction of unchanged cuprous oxide in solid solution in the metal, which may be the real effective catalytic agent, or for some other cause as yet unknown. Consequently, experimenters have had recourse to elevation of the temperature to enhance the diminishing activity. At 300° the second stage of the thermal decomposition into carbon monoxide and hydrogen is quite marked, whilst at 350° it is practically complete in presence of metallic copper at low space velocities:

$$H \cdot CHO = CO + H_2$$
$$\text{and } CH_3 \cdot OH = CO + 2H_2$$

The second reaction is reversible and has been made use of for the synthesis of methyl alcohol from water gas (see pp. 257, 258). Sabatier and Senderens[2] investigated the catalytic activity of other metals and oxides on the dehydrogenation of methyl alcohol with the following results:

Substance	Temperature Commencement of Dehydrogenation	Temperature of Maximum Activity	Loss of Formaldehyde due to Secondary Decomposition
Nickel	180°	360	Above 60 per cent
Cobalt	Slightly more active than nickel, but less than copper.		
Iron	Slightly less active than cobalt		
Platinum	250°	-	Complete
Manganese oxide	320	360	Small
SnO_2	260	350	Small, but reduction to metal takes place
CdO	250	300	Complete

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[1] See *La Catalyse en chimie organique* and *Ann. Chim. Phys.*, 1910, **20**, 344.

[2] *Ann. Chim. Phys.*, 1905, **8**, 1473.

The following catalytic oxides suitable for dehydrogenation of methyl alcohol in order of increasing activity are cited by Sabatier. The optimum temperature for dehydrogenation appears to be 350°:

$$\mathrm{GlO.\ SiO_2,\ TiO_2,\ ZnO,\ ZrO_2.\ MnO.\ Al_2O_3.}$$

The use of bauxite for this purpose might possess certain advantages.

It was therefore evident that the usual process of fractional combustion of methyl alcohol was actually based on the primary catalytic dehydrogenation of the alcohol into aldehyde and hydrogen, whilst the addition of oxygen might be regarded as necessary to maintain the temperature of the reaction (28 cals being absorbed per grm. mol. in the dehydrogenation process), to lower the partial pressure of the hydrogen, and possibly to revivify the copper catalytic material by continuous alternate oxidation and reduction. E. I. Orloff[1] confirmed nearly all Sabatier's experiments, showing that the following catalysts were effective in the dehydrogenation process. Copper precipitated on asbestos, cerium sulphate, and thorium oxide, platinum black, metallic platinum, coke containing precipitated copper, vanadium oxide on asbestos. Unsatisfactory results were obtained with iron, practically complete decomposition to oxides of carbon and lamp-black occurring.

In his later communications Orloff advises the addition of air and recommends copper gauze preceded by platinised pumice or platinised asbestos, and states that the best conversion is effected when the reaction proceeds without the application of external energy and that the following relationships are obtained:

Ratio.	
O_2 : MeOH . .	·01 : 1
Alcohol : Total volume gaseous mixture . .	·0342 : 1
$\dfrac{\text{Concentration of oxygen} \quad \text{concentration of alcohol vapour}}{\text{Square of mean velocity of gas flow}}$	0·00103

Le Blanc and E. Plaschke[2] similarly conducted a series of experiments on fractional combustion of methyl alcohol, using silver wire gauze and electrolytically silvered copper gauze as catalysts; they also arrived at the conclusion that the process is virtually one of dehydrogenation and that the function of the oxygen was merely to revivify the catalytic material, for which purpose freshly reduced copper was most suitable. Their most favourable yields were 58 per cent with silver and 55·4 per cent with copper, under the following experimental conditions:

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[1] *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 855, 1023, 1414, 1908, **40**, 796.

[2] *Zeitsch. Elektrochem.*, 1911, **17**, 151

Length of Silver Gauze Spiral in cm	Grm O_2 per grm Alcohol	Temp of Catalyst	Velocity of Air in litres per minute
5·85	0·459	455	2·669*
Per cent Conversion	**Per cent Unchanged**	**Per cent Loss**	**Diameter of Tube**
58·06	26·43	15·51	30 mm

* Representing a space velocity referred to the air of 3900 (litres of air per litre of catalyst space per hour)

The effluent gas contained the following proportions of CO_2, CO, and H_2 respectively 4·46, 4·16, and 11·49 per cent

The figures represent the optimum yield obtained after alteration of all the independent variables one at a time

Fokin[1] continued Orloff and Le Blanc's researches and obtained the following orders of activity for the conversion in the passage of alcohol-air mixtures over different metals

Ni	1·08 per cent	Cu	43·47 per cent
Al	1·5 „	Ag	64·60
Mn	2·01 „	Au	71
Co	2·8 „	CuAg alloy	84
Pt	5·2 „		

It will be noted that silver is extremely effective

Bouhard[2] suggests the use of silver precipitated on flax as support material, whilst O Blank[3] suggests silver on asbestos

Hochstetter[4] has attempted to produce a catalytic material which should accelerate both reactions viz the dehydrogenation process, $CH_3\cdot OH = H\cdot CHO + H_2$ as well as the fractional combustion, $2CH_3\cdot OH + O_2 = H\cdot CHO + H_2O$ Thus, he states that he has obtained the following results by using metal couples instead of the pure metals

	Per cent Yield
Pure Cu	70
Cu alloyed with 1/10,000 Pt	72
Cu coated with 1/10 000 Pt	77
Ag	75
Ag with a Cu tube	84
Ag coated with 1/10,000 rhodium	96
Ag „ „ 1/10,000 Pt	96

Other suggested methods of preparation of formaldehyde have been the subject of patent literature

Both the Badische[5] and Dreyfus[6] patents suggest passing a mixture of carbon monoxide and hydrogen in the ratio of 2 : 1 at 100 atmospheres pressure over catalytic materials (such as Pt, Cu Fe, Cr Ni, Ce, Ur, V, or their oxides) at 300°-400° (See further, pp 257, 258)

Brodie,[7] Losanitsch, and Jovitschitsch[8] obtained small quantities of formaldehyde from these gases when subjected to the silent electric discharge, Chapman and Holt [1] by the high-tension electric discharge, whilst de Jahn proved the presence of aldehyde when CO and H_2 were passed over spongy platinum into water [2]

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[1] *J Russ Phys Chem Soc* 1913, **45**, 286

[2] F P 412501, 1910

[3] *J Soc Chem Ind*, 1911, **30**, 49

[4] B P 464 1914

[5] B P 20486 1913

[6] B P 108855 1915

[7] *Proc Phys Soc*, 1874, **12**, 171

[8] *Ber*, 1897, **30**, 135

The thermal decomposition of dimethyl ether, tin formate,[3] and calcium formate, as well as the fractional reduction of formic acid by hydrogen over iron or nickel catalysts at 300° to 500°,[4] are all suggested methods for the preparation of formaldehyde.

Equally interesting and worth attention are the various suggestions for the fractional combustion of methane into methyl alcohol or formaldehyde.

Glock,[5] in 1898, suggested the passage of a mixture of methane and air over granulated copper or pumice maintained at 800°, the process, being circulatory, removing the formaldehyde after each cycle by a system of scrubbers Lance and Elsworthy [6] suggest the use of hydrogen peroxide or persulphuric acid as an oxidant in the presence of ferrous sulphate, presumably as a catalytic material The Sauerstoff u Stickstoff Ind [7] and V. Unruh [8] claim the use of tan bark as catalyst, stating that oxidation of methane by air will take place at 30–50° in the presence of such material It is more than probable that the aldehyde was itself derived from the tan bark under the conditions of operation Fernekes [9] describes a special combustion furnace for the fractional oxidation of methane, whilst Otto [10] suggests the use of ozone as an oxidant Lacy [11] describes the direct chemical conversion process, $CH_4 \rightarrow CH_3Cl \rightarrow CH_3 \cdot OH$, whilst Lance and Elsworthy [12] claim the production of methylamine by hydrogenation of hydrocyanic acid over a metal catalyst with subsequent decomposition of the amine with steam in the presence of a catalyst

$$CH_3 \cdot NH_2 + H_2O \rightarrow CH_3 \cdot OH + NH_3$$

Bone and Wheeler showed that a 20 per cent yield could be obtained by the flameless combustion of methane on borosilicate glass beads.

The fractional oxidation of other alcohols can be accomplished in like manner Thus, glycerine in the presence of air will give small quantities of glycerine aldehyde in the presence of platinum black, ethyl alcohol and air passed over platinised pumice at a dull red heat yields 16·8 per cent of acetaldehyde eugenol in a similar manner yields 2·9 per cent of vanillin It will, however, be noted that the yield of aldehyde is invariably small when the process of fractional combustion is adopted, whilst the catalytic dehydrogenation processes, on the other hand, usually give good yields with very small losses.

The partial oxidation of hydrocarbons. In view of the technical importance of the conversion of the hydrocarbons, both aromatic and aliphatic, into the more valuable oxidation products, numerous attempts have been made to effect such partial oxidation with air as oxidising agent in the presence of various catalytic agents.

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[1] *J. Chem. Soc.*, 1905, **87**, 916

[2] *Ber.*, 1889, **22**, 989.

[3] B.P. 183856

[4] Badische Co Pat. 185932.

[5] D.R.P. 107014. See also D.R.P. 286731

[6] B.P. 7297/1916

[7] D.R.P. 214155/1906.

[8] U.S.P. 891753/1907.

[9] U.S.P. 1038546/1912

[10] *Ann. Chim. Phys.*, 1898 (vii), **13**, 77.

[11] B.P. 16194/1914.

[12] B.P. 4409/1906

These methods naturally divide themselves into those in which liquid phase and those in which vapour phase oxidation is made use of. Although in catalytic hydrogenation both liquid and vapour phase catalytic reduction have proved successful, in catalytic oxidation only the latter has been developed to the technical stage.

In the case of hydrocarbons of the aromatic series Wedge[1] claimed the liquid phase oxidation of benzene to phenol, utilising platinum black as catalytic agent, whilst Willstatter and Sonnenfeld[2] describe the use of platinum as a catalyst in the fractional oxidation of cyclohexanol to adipic acid. More attention has been paid to the liquid phase fractional oxidation of the long chain aliphatic hydrocarbons with a view to the production of synthetic fats. Grun[3] and Fischer and Schneider[4] have noted that oxidation proceeds slowly at the melting point of the wax, the reaction velocity increasing with rise in temperature. An upper limit of *circa* 150° C. is set to the temperature so as to avoid as far as possible the degradation of the long chain aldehydes, alcohols, and acids produced by further oxidation. A 50 per cent. yield of odd-numbered chain fatty acids may be obtained by low-temperature oxidation of several months' duration. The reaction appears to be somewhat complicated, since the formation of unsaturated oxy-derivatives always occurs, and the course of the oxidation can in fact be followed by the determination of the iodine value. The reaction is slightly autocatalytic in action, since the seeding of a fresh wax with a partially oxidised fraction accelerates the oxidation, at least in the primary stages.

Many attempts have been made to accelerate this low-temperature oxidation process by the addition of catalysts, notably by alkalis and various oxygen carriers such as salts of iron and manganese. The results, however, appear to be inconclusive.

More successful have been the processes of fractional oxidation of volatile hydrocarbons in the vapour phase. We have already referred to the production of formaldehyde by the partial oxidation of methane. Sabatier and Mailhe[5] have shown that small quantities of aldehydes and alcohols can be produced by the catalytic combustion of paraffinoid hydrocarbons, whilst similar results were obtained by Orloff[6] utilising copper oxide gauze as catalytic agent. The first attempts to oxidise aromatic hydrocarbons catalytically were made by Coquillon,[7] who noted the production of both benzaldehyde and benzoic acid on the passage of either benzene or toluene vapour and air over an incandescent platinum wire. Walter showed[8] that benzoic acid and benzaldehyde would readily be produced by the fractional oxidation of toluene and anthraquinone from anthracene, utilising vanadium pentoxide as catalytic agent[1] Coke[2] and chromium oxide[3] have been suggested for similar purposes. Weiss and Downs[4] have investigated in detail the conditions for the fractional oxidation of naphthalene to phthalic anhydride and the formation of maleic anhydride from benzene It is interesting to note that small quantities both of phenol (0·3 per cent) and benzoquinone were obtained from benzene In the presence of steam and at high pressures diphenyl was likewise obtained in moderate amount. The most effective catalyst was found to be vanadium pentoxide[5]

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[1] B.P. 2010 1901.

[2] *Ber.*, 1913, **46**, 2952.

[3] *Ibid.*, 1920, **53**, 987.

[4] *Ibid.*, 1920, **53**, 922.

[5] *Compt. rend.*, 1906, **142**, 1394.

[6] *J. Russ. Phys. Chem.*, 1907, **39**, 855, 1023; 1908, **40**, 1414.

[7] *Compt. rend.*, 1875, **80**, 1089.

[8] *J. pr. Chem.*, 1892, **107**, 111.

The difficulties successfully overcome by Weiss and Downs are those inherent in such processes of oxidation of organic substances, namely, those of temperature control. These are apparent from the following data on the thermal values of three typical catalytic gaseous oxidation processes:

Reaction	Optimum Temperature of Catalysis	Optimum Air Reactant Ratio by Volume	Heat developed B.T.U. per lb of Reactant	Heat Capacity of entering Gases at 25° C at Optimum
$SO_2 \rightarrow SO_3$	400° C	7·5 : 1	635	661
$NH_3 \rightarrow NO$	750° C	10 : 1	5,660	6260
$C_6H_6 \rightarrow$ Maleic anhydride	400° C	22·5 : 1	10,560	1620

It will be observed that provision has to be made for the dissipation of heat sixteen times greater than that evolved in the oxidation of sulphur dioxide, and that in addition local elevation of temperature has to be avoided, as the reactions of fractional oxidation are not reversible as is the case in the sulphur dioxide-trioxide equilibrium

Oxidation at charcoal surfaces. In view of the biological importance of low-temperature surface combustion many experiments have been made with charcoal as a catalyst for the oxidation of organic materials.

The results of numerous investigations on the adsorption of oxygen by charcoal, notably by Baker,[6] Dewar,[7] Rhead and Wheeler[8] indicate that oxygen may be adsorbed on a charcoal surface to form at least three types of surface compounds which may be associated with the diamond, paraffin, and ethenoid portions of the surface. One form is removable only at high temperatures as oxides of carbon, another removable as oxides of carbon by evacuation or by fusion with sodium carbonate,[9] and a third which can, under certain conditions, be recovered as oxygen. This last form is endowed with catalytic properties, for not only does low-temperature autoxidation occur but many processes of oxidation are catalytically accelerated. Calvert[1] noted the oxidation of ethyl-alcohol vapour and gaseous hydrocarbons, a result confirmed by Firth.[2] Feigel[3] noted the catalytic oxidation of solutions of sulphides, chromates and iodides. Warburg and his co-workers have examined the catalytic oxidation of oxalic and certain α amino acids,[4] Meyerhof the oxidation of glucose in the presence of phosphoric acid,[5] Freundlich and Bjerke[6] the oxidation of phenylthio-carbamide, and Rideal and Wright[7] that of malonic acid.

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[1] See also D.R.P. 168291/1904; F.P. 360785/1905, and B.P. 21941/1905

[2] Woog, *Compt rend*, 1907, **145**, 174.

[3] Lowenthal, D.R.P. 239651/1909.

[4] U.S.P. 1318631, 2, and 3/1919.

[5] *J Ind. Eng Chem*, 1920, **12**, 228

[6] *J. Chem. Soc*, 1889, **51**, 219.

[7] *Compt rend*, 1904, **139**, 201

[8] *J. Chem. Soc.*, 1913, **103**, 461, 1210.

[9] Taylor, *J. Amer Chem. Soc.*, 1921, **43**, 2059.

The autoxidation process is found to be of zero order and independent of the oxygen pressure over a considerable range at high pressures, with a temperature coefficient of $\frac{k_{50}}{k_{10}} = 1·80$. By selective poisoning Rideal and Wright found that with an active sugar charcoal of mean surface area of 266 cm.² per milligrm. only 0·38 per cent of the surface was autoxidisable.

The oxidation of acids such as oxalic acid proceeds over a relatively much greater area: thus, for the particular form of charcoal viz. sugar charcoal, the fraction catalytically active in effecting the oxidation of oxalic acid was found to be 10·5 per cent. Both acid and oxygen are adsorbed, the reaction velocity rising to a maximum and falling again as the concentration of oxalic acid is increased. The optimum velocities were obtained at a concentration of 0·0075 molar oxalic acid and 0·050 molar malonic acid, with a temperature coefficient of $\frac{k_{50}}{k_{10}} = 2·0$.

The reaction velocity as a function of the concentration of the reactants was found to be expressible in the form

$$\frac{dx}{dt} = \frac{K\sqrt{P_0}\,C_x}{(1 + m\sqrt{P_0} + nC_x)^2},$$

which reduces to the simpler forms

$$\frac{dx}{dt} = K'C_x\sqrt{P_0}$$

for small oxalic concentrations, and to

$$\frac{dx}{dt} = K''\frac{\sqrt{P_0}}{C_x},$$

for high concentrations of acid, both being experimentally realised for a number of such surface oxidations.

Such charcoals can readily be activated or promoted by heat treatment with urea and iron salts or dye-stuffs and iron salts.

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[1] *J. Chem. Soc.*, 1867, **20**, 293.

[2] *Trans. Farad. Soc.*, 1924, **20**, 370.

[3] *Zeitsch. anorg. Chem.*, 1921, **119**, 305.

[4] *Pflüger's Archiv*, 1914, **155**, 547; *Biochem. Zeitsch.*, 1921, **113**, 257; 1924, **145**, 461.

[5] *Biochem. Zeitsch.*, 1923, **135**, 558.

[6] *Zeitsch. physiol. Chem.*, 1916, **91**, 31.

[7] *J. Chem. Soc.*, 1925, **127**, 1347.

It is found that this treatment brings about two distinct changes in the surface; firstly, a general extension, of which a large portion possesses approximately the same specific catalytic activity as the original charcoal. In addition a small portion, only some 2·0 per cent. of the surface is extremely active, and owing to the sensitivity of these portions to poisoning by potassium cyanide it is probable that these portions are the true promoted iron charcoal systems.

These reactions afford an excellent example of the two effects of promoters discussed in Chapter III.

The Preparation of Acids

The further oxidation of the aldehydes into the corresponding acids by a catalytic process has been successfully developed in the case of acetaldehyde; as catalyst, manganese acetate, or more rarely the formate, butyrate, lactate, or benzoate, dissolved in acetic acid is employed in the proportion of 300 kilos of aldehyde to 3 kilos. of manganese acetate. Aeration is accomplished under pressure, and the aldehyde is converted practically quantitatively into acetic acid. Several difficulties were associated with the earlier phases of the process. The reaction is strongly exothermic, and a very efficient cooling system has to be employed; at the same time a sufficient depth of liquid to ensure proper aeration must be maintained. All metals sufficiently robust to stand the pressures employed are rapidly attacked under the combined influence of oxygen and acetic acid, thus entailing a heavy repair bill. Pure aluminium liners are frequently employed. The most serious difficulty is the danger of explosion associated with the formation of the extremely unstable peracetic acid, $CH_3.CO.OOH$, under continued aeration in the presence of the manganese salt; over-aeration has thus to be carefully avoided. Grunstein and Behrens have shown that other catalytic substances, such as the oxides of vanadium, uranium, cerium, and iron, possess an activity equal to that of the manganese salts,[1] but that their use is attended with a greater risk of explosion, since these salts are not specially active in the removal of the peracetic acid by reduction with aldehyde, according to the equation

$$CH_3.CO.OOH + CH_3.CHO = 2CH_3.COOH,$$

a reaction which is accelerated by manganese. In technical working a 30 per cent loss occurs, due to further oxidation of the acetic acid to carbon dioxide and water.

Ethyl alcohol can be directly oxidised to acetic acid by admixture in the vapour state with air and passage over platinum black or vanadium pentoxide.

The preparation of oxalic acid by the oxidation of sugar and starches is no longer accomplished by means of hot nitric acid, which entails a very considerable loss in the form of carbonate, tartaric, mucic, and saccharic acids, but use is made of the observation[1] of Naumann, Moeser, and Lindenbaum that the addition of 0 2 per cent of vanadic oxide effects the conversion almost quantitatively in the cold in from ten to twenty hours.

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[1] *Compt. rend.*, 1907, **145**, 124.

THE USE OF CATALYTIC OXIDATION PROCESSES IN THE DYE INDUSTRY

Aniline black.—The preparation of aniline black, one of the most important dyes for cotton yarns was first developed by John Lightfoot, of Accrington, in 1863, and is now largely employed in all the dyeing industries

The constitution of the dye was proved by A G Green,[2] who contributed a very important addition to the number of catalytic oxidation processes of technical importance Aniline black is essentially an oxidation product of aniline, during its course of oxidation, three distinct stages of oxidation can be observed

(1) Emeraldine, which is blue in the form of the free base and gives green salts

(2) Nigraniline, which is a dark blue base and gives blue salts

(3) Ungreenable black or aniline black

According to Green, oxidation proceeds by a series of quinonoid additions in the following order

$$C_6H_5\ NH_2 + C_6H_5\ NH_2$$

$$\downarrow$$

$$C_6H_5\ N\ C_6H_4\ NH$$

(Caro's yellow imide)

$$\downarrow \ \text{Direct quinonoid addition (acid conditions)}$$

$$C_6H_5\ NH\ C_6H_4\ NH\ C_6H_4\ N\ C_6H_4\ NH$$

(Willstatter's blue imide)

$$\downarrow \ \text{Oxidation}$$

$$C_6H_5\ N\ C_6H_4\ N\ C_6H_4\ N\ C_6H_4\ NH$$

(Willstatter's red imide)

$$\downarrow$$

$$C_6H_5\ N\ C_6H_4\ N\ C_6H_4\ N\ C_6H_4\ N\ [C_6H_4\ NH]_3\ C_6H_4\ NH_2$$

Emeraldine

$$\downarrow \ \text{Oxidation}$$

$$C_6H_5\ N\ C_6H_4\ N\ [C_6H_4\ N\ C_6H_4\ N]_2\ C_6H_4\ NH\ C_6H_4\ NH_2$$

$$\downarrow \ O_2$$

$$C_6H_5\ N\ C_6H_4\ N\ C_6H_4\ N\ C_6H_4\ N\ C_6H_4\ N\ C_6H_4\ N\ C_6H_4\ NH\ C_6H_4\ NH_2$$

Nigraniline

$$+ C_6H_5 . NH_2 . HCl$$

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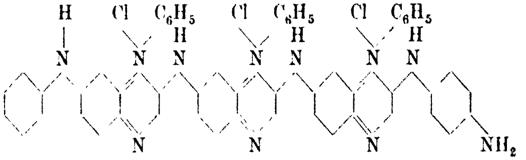
[1] B P 17424-1911

[2] *J pr Chem* (ii), 1907, **75**, 146



Aniline black.

The usual oxidising agents employed are bichromates or sodium chlorate, whilst copper sulphate, copper sulphide (prepared by the double decomposition of copper sulphate and sodium sulphide), or vanadium chloride are used as catalysts.

For example, a 15 per cent aniline hydrochloride solution (neutralised with free base), with 5 per cent of sodium chlorate as oxidising agent, is mixed with 5 per cent of a 54 per cent copper sulphide paste to form an effective dyeing-bath. The quantity of vanadium salt required to exert the same catalytic activity as the copper salts normally employed is far less Sabatier[1] states that only 1 part in 70,000 parts of aniline is required; Witz estimates the ratio at 1 : 270,000, whilst the following is the composition of a dye-bath actually employed.

Parts by weight :

8 per cent aniline hydrochloride.
1·5 per cent aniline.
4 per cent sodium chlorate.
5 per cent vanadium salt solution.

The solution of the catalytic material is made as follows : 8 grms. of ammonium vanadate are dissolved in 40 grms. of 30 per cent hydrochloric acid and 80 c.c. of water. Ten grms of glycerin are added, and the whole is made up to 2 litres. The ratio aniline salt to vanadium salt is approximately 47,500 : 1. This dyeing-bath is, it is stated, not so good as the copper sulphide catalyst bath, since it is rather too rapid in operation, and part of the dye is deposited in the solution itself or loosely adherent to the fibre.

Green,[2] in 1907, made the interesting discovery that bichromate and chlorates could be replaced by air as oxidising agent provided that certain promoters were added to the catalytic agents usually employed. In this way a considerable economy in materials was effected, and all tendering of the fibre occasioning weakening due to the formation of the oxycelluloses was avoided.

As promoters, small quantities of a *p*-diamine or *p*-amidophenol were found most effective. The use of amidophenol, *p*-phenylenediamine and its sulphonic and carboxylic derivatives, dimethyl-*p*-phenylenediamine, *p*-amidophenylaniline, benzidine, diamidodiphenylaniline, quinone, mono- and di-imides and their chlorides, *p*-nitrophenol, nitrodimethylaniline, *p*-amidophenylquinonimide and their homologues and derivatives, is claimed.

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[1] *La Catalyse.*

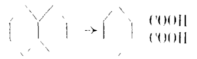
[2] B.P. 16189/1907.

The addition of 4 per cent of the promoter on the weight of aniline taken is said to be sufficient. The mechanism of operation has not been fully explained, but the catalyst probably hastens the oxidation process by the intermediate formation of complex indamines. Iron, cerium, uranium, and osmic salts exert similar catalytic activity in this oxidation process, but have not received technical application.

Methyl-violet and fuchsine. Cupric chloride and small quantities of phenol are frequently added in the oxidation of dimethylaniline to methyl-violet. It is said that with suitable proportions of catalyst and promoter (phenol) the oxidation can be effected with atmospheric oxygen in lieu of the sodium chlorate usually employed.

In the oxidation of aniline and *o*- and *p*-toluidine to fuchsine nitrobenzene can be used as oxidising agent in the presence of a small quantity of a vanadium salt or slightly larger quantities of ferric chloride.

Indigo. Heumann's synthesis of indigo, which was successfully developed by the Badische Co., was based upon the primary conversion of crude naphthalene into phthalic acid, utilising fuming sulphuric acid as an oxidant.



It may be noted in passing that the growth of the contact sulphuric-acid process in Germany was determined by the demand for fuming sulphuric acid in the production of this dye.

Groebe[1] accidentally discovered that mercury was an effective catalytic agent in this process of oxidation between 200° and 300°. Further investigation, singularly enough, proved that mercuric sulphate was one of the most effective; copper sulphate, although exerting a reasonable catalytic activity, is inferior, although a mixture of copper and mercuric sulphates is superior to either constituent used singly.[2] Nickel and iron are slightly active, whilst the salts of manganese, potassium, and magnesium are inactive.

The use of a small globule of mercury or a strip of copper in the usual Kjeldahl process of nitrogen estimation is a striking application of these catalysts to the oxidation of nitrogenous organic matter by strong sulphuric acid.

The patents of Rosenthal[3] also illustrate the oxidising action of mercury salts. The 10 per cent yield of tertiary bases of the aromatic group obtained by oxidation of tertiary aromatic amines with sulphuric acid at temperatures above 200° is increased to a 60 per cent yield in presence of mercury.

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[1] *Ber.*, 1896, **29**, 2806.

[2] Bredig and Brown, *Zeitsch. physikal. Chem.*, 1903, **46**, 502.

[3] D.R.P. 127179 and 127180.

AUTOXIDATION AND INDUCED OXIDATION

The investigations on the direct oxidation by means of oxygen gas of a number of organic substances has indicated that the process cannot take place by means of a simple addition, *e.g.*

$$2X + O_2 \rightarrow 2XO,$$

where X is the substance undergoing oxidation to the stable oxide XO. The classic researches of Schonbein [1] indicated clearly that, in many cases of oxidation, for every molecule of oxygen consumed a molecule of oxygen was simultaneously converted into a more active state; this active oxygen could then secondarily react either with more oxygen to form ozone, with water to form hydrogen peroxide, or in the presence of other oxidisable substances could oxidise them, frequently causing oxidations which cannot be accomplished by ordinary atmospheric oxygen. For example, hydrogen peroxide is formed during the rusting of lead, zinc, and probably iron; ozone is formed during the oxidation of phosphorus. Indigo is converted into isatin during the autoxidation of palladium hydride, benzaldehyde, or turpentine. Various of the more important theories which have been advanced to explain the mechanism of these processes may be briefly classified as follows.

The dualistic theory. Schonbein [2] was of the opinion that these cases of autoxidation were best interpreted on C. Brodie's [3] hypothesis, in which ordinary oxygen during the process of oxidation is split up into two parts, 'ozone' and 'antozone':

$$O_2 \begin{array}{l} +O, \text{ or ozone} \\ -O, \text{ or antozone} \end{array}$$

R. Clausius [4] more definitely stated that Brodie's ozone and antozone could be regarded as atomic oxygen of opposite electric charges:

$$O_2 \rightarrow \dot{O} + O'.$$

Van 't Hoff,[5] as a result of his experiments on the autoxidation of phosphorus, introduced the hypothesis that atmospheric oxygen is, already prior to any process of oxidation, normally partly dissociated into charged atomic oxygen, and that the equilibrium $O_2 \rightleftarrows \dot{O} + O'$ must be considered as an important factor in oxidation phenomena.

According to the above hypothesis, all processes of autoxidation are dual in character, two substances simultaneously undergoing oxidation. Engler [6] has attempted to distinguish between these by terming the substance undergoing oxidation the autoxidiser, and the substance simultaneously oxidised the acceptor. It is evident that either the autoxidiser or the acceptor may react, on the one hand, with the ozonic, or, on the other, with the antozonic form of the active oxygen, depending on the chemical nature of the substances undergoing oxidation; thus water, phosphorus, the alkali metals, and the alkaline-earth metals form antozonides on oxidation, whilst ozone and the chromates, permanganates, hypochlorites, and vanadates, as well as lead, zinc, nickel, bismuth, silver, and manganese oxides, are ozonides.

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[1] *J. pr. Chem.*, 1858-1868, 73-99.

[2] *Loc. cit.*

[3] *Phil. Trans.*, 1850, **141**, 759 *et seq.*

[4] *Pogg. Ann.*, 1858, **103**, 644.

[5] *Zeitsch. physikal. Chem.*, 1895, **16**, 411.

[6] *Kritische Studien uber die Autoxydationsvorgange*, Braunschweig, 1903.

Van 't Hoff noticed that in the case of phosphorus undergoing atmospheric oxidation in the presence of indigo acting as acceptor, a continuous supply of fresh acceptor was required to maintain the velocity of oxidation up to a measurable speed. He consequently argued that the reaction $O_2 \rightleftarrows O + O'$ must be a reversible one, since the accumulation of the ozonic form of active oxygen normally removed in the oxidation of the indigo to isatin retarded the action of the antozonic oxygen on the phosphorus.[1]

It must be admitted that a search for the charged ozonic modification of oxygen which should be present in the air after passage over phosphorus has yielded conflicting results. Elster and Geitel[2] noted that air thus treated was electrically conducting,[3] and Goekel[4] showed that this conductivity was not due to the presence of ozone, which could be absorbed without destroying the conductivity. Barus,[5] Harms,[6] and Bloch,[7] on the other hand, have shown that the conductivity cannot be attributed to the ozonic oxygen or charged ionic oxygen, but is due to oxides of phosphorus collected round charged nuclei forming aggregates of relatively large dimensions ($r = 10^{-6}$ cm.), whilst the actual number of charged ions observed fell far short of the stoichiometric ratio, oxygen absorbed : oxygen ionised = 1 : 1, postulated by the hypothesis.

E. Hoppe-Seyler[8] and Baumann adopted the same hypothesis as Schonbein, but substituted the term "nascent" oxygen for Schonbein's ozonides and antozonides; according to these investigators, processes of autoxidation may be represented by the general equation

$$X + O_2 \longrightarrow XO + \text{nascent oxygen}$$

and such nascent oxygen was to be regarded as possessing superior activity to the substance in the ordinary molecular state. It is evident that the difference in view is one of nomenclature rather than of principle.

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[1] See J. Joubert, *Thèse sur la phosphorescence du phosphore*, 1874; T. Ewan, *Phil. Mag.*, 1894 (v.), **38**, 512; J. Chappuis, *Bull. Soc. chim.*, 1881 (ii.), **35**, 419.

[2] *Wied. Ann.*, 1890, **39**, 321; *Physikal. Zeitsch.*, 1903, **4**, 457.

[3] See also Matteucci, *Encyc. Brit.*, 1855, **8**, 622; Naccari, *Atti delle Scienze di Torino*, 1890, **25**, 252.

[4] *Zeitsch. physikal. Chem.*, 1903, **4**, 16.

[5] *Experiments with Ionised Air*, Washington, 1901.

[6] *Zeitsch. physikal. Chem.*, 1902, **3**, 111.

[7] *Ann. Chim. Phys.*, 1905 (viii.), **4**, 25.

[8] *Zeitsch. physiol. Chem.*, 1878, **2**, 22.

The intermediate compound theory.—M. Traube,[1] Gisammetti,[2] A. Bach,[3] C. Engler and V. Wild,[4] and others developed the hypothesis of the intermediate compound.

Thus, according to M. Traube, the process of autoxidation of the metals with the simultaneous formation of hydrogen peroxide takes place through the presence of water as intermediary, as represented by the equation

$$M + OH_2 + O_2 \longrightarrow MO + H_2O_2.$$

Hydrogen peroxide is thus reduced oxygen, and not oxidised water as postulated by Schonbein and his co-workers. The curious reducing actions of hydrogen peroxide, *e.g.*

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2,$$

are cited to support this claim.

According to Traube, the stoichiometric ratio

$$MO : H_2O_2 :: 1 : 1$$

need not necessarily be observed in practice, as the secondary reaction

$$M + H_2O_2 = M(OH)_2$$

may take place. Such a reaction is extremely unlikely, and the usual discrepancy between the theoretical quantity of peroxide and that actually obtained must be put down to thermal decomposition.

The necessity for the presence of at least small quantities of water vapour in processes of combustion[5] has been observed by many independent investigators, and its function as an intermediary catalyst or electrolyte to complete the voltaic circuit need not be discussed at this point. The application of this principle to explain certain cases of autoxidation and induced oxidation forms an important extension of the hypothesis. It will be noted that the formation of substances such as ozone, permanganate, and the oxides of the heavy metals, *i.e.* Schonbein's ozonides, must be considered as secondary reactions taking place between the hydrogen peroxide and the acceptor. In some cases, as, for example, in the formation of ozone from oxygen and hydrogen peroxide, or of silver oxide from hydrogen peroxide and silver, this assumes exceedingly improbable reactions.

A. Bach adopted another point of view, in which an intermediary peroxide was first formed, prior to the decomposition into an oxide and with simultaneous oxidation of the acceptor. Thus, in the oxidation of a metal in the *presence of water, a metallic oxide and hydrogen peroxide are assumed to be formed according to the following scheme*

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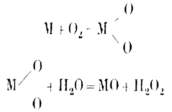
[1] *Ber.*, 1882, **15**, 663 ; 1893, **26**, 1471.

[2] *Abhandlungen*, Berlin, 1899.

[3] *Compt. rend.*, 1897, **126**, 2, 951.

[4] *Ber.*, 1897, **30**, 1669.

[5] See Mrs. Fulhame, *An Essay on Combustion*, London, 1794. H. B. Dixon, *Phil. Trans.*, 1884, **175**, 630 ; *J. Chem. Soc.*, 1886, **49**, 95, and H. E. Armstrong, *Brit. Assoc. Reports Proc. Roy. Soc.*, 1886, **40**, 287.

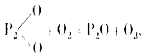


$$M + O_2 = M\genfrac{}{}{0pt}{}{O}{O}$$

$$M\genfrac{}{}{0pt}{}{O}{O} + H_2O = MO + H_2O_2$$

In the oxidation of phosphorus with the simultaneous production of ozone we may adopt the equations of Engler and Wild,[1] or of Ostwald [2] to explain the mechanism on Bach's intermediate peroxide theory

$$(a)\quad 2P + O_2 = P_2O_2$$



$$P_2\genfrac{}{}{0pt}{}{O}{O} + O_2 = P_2O + O_3,$$

$$(b)\quad 2P + 2O_2 = P_2O_4 = P_2O + O_3,$$

giving the stoichiometric ratio $P : O_2 = 2 : 1$ the ratio actually obtained by van 't Hoff

Bodlander,[3] and Baeyer and Villiger,[4] in researches on the oxidation by air the actor, of benzaldehyde the inductor, with indigo as an acceptor, gave additional support to Bach's theory by the isolation of an intermediary peroxide, benzoyl hydrogen peroxide

$$C_6H_5 \cdot CHO + O_2 = C_6H_5 \cdot CO \cdot O(OH),$$

which peroxide could then react in two distinct ways

(*a*) With another molecule of benzaldehyde,

$$C_6H_5 \cdot CO \cdot O(OH) + C_6H_5 \cdot CHO \rightarrow 2C_6H_5 \cdot COOH$$

(*b*) With the acceptor indigo,

$$C_6H_5 \cdot CO \cdot O(OH) + \text{indigo} \rightarrow C_6H_5 \cdot COOH + \text{isatin}$$

The hypothesis of a primary formation of an unstable peroxide of the inductor has been further strengthened by isolation of such salts in the case of cerium oxide by Job,[5] and in the case of ferric and ferrous iron by Manchot,[6] Goard and Rideal [7] Bohnson and Robertson [8]

It is clear that this hypothesis may be extended in the following manner The primary reaction between inductor and oxygen to form an unstable peroxide may be represented as follows

$$(1)\quad A + O_2 \dashrightarrow AO_2$$

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[1] *Ber*, 1897, **30**, 1669

[2] *Zeitsch physikal Chem*, 1900, **34** 250

[3] *Ahrens Sammlung*, 1889, **3** 470

[4] *Ber*, 1900 **33** 585, 3480

[5] *Ann Chim Phys*, 1900 (vii), **20**, 205, *Compt rend* 1902 **134** 1052

[6] *Zeitsch anorg Chem*, 1901, **27** 397, *Ber*, 1901, **34**, 2479

[7] *Proc Roy Soc* (A), 1924, **105** 150

[8] *J Phys Chem*, 1921, **25**, 19, *J Amer Chem Soc*, 1923, **45**, 2493

The peroxide AO_2 may then react with another molecule of A,

$$(2) \quad A + AO_2 \rightarrow 2AO$$

a view supported by Moureu in his extensive researches on the mechanism of inhibition of these autoxidations.

Alternately the peroxide AO_2 may react with the acceptor B,

$$(3) \quad B + AO_2 \rightarrow AO + BO,$$

to form stable oxides both of A and of B.

In some cases the oxide AO may be again reduced by B to the inductor A.

$$(4) \quad AO + B \rightarrow A + BO.$$

In the case of reactions proceeding to the stage (3) the final result of oxidation is evidently the complete oxidation of the acceptor B to the stable oxide BO. For every molecule of B undergoing oxidation at least one molecule of A has undergone a similar process, but if a reaction according to (2) can take place, more inductor than acceptor will be found oxidised in the system.

In addition to the cases cited above, the following examples indicate the diversity of these coupled reactions.

Actor	Inductor	Acceptor
$HgCl_2$	Na_2SO_3	Na_3AsO_3
O_2	$Ce(OH)_3$	$Ni(OH)_2$
O_2	Na_2SO_3	Na_3AsO_3
O_2	$SnCl_2$	$Fe(NH_4)_2SO_4$
O_2	Na_2SO_3	$NaNO_2$

The conditions under which a coupled reaction consisting of two reactions exemplified by Equations (1) and (3) may be converted into a catalytic reaction in which the inductor A becomes a catalyst, as is indicated by Equation (4), have been investigated by Goard and Rideal,[1] who showed that if the oxidation potentials of the system conformed to the following scheme:

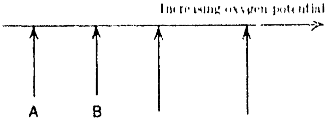

FIG 14

the reaction was coupled; whilst reduction of the oxidised inductor AO would be achieved and the reaction rendered catalytic, in that the inductor would function as a catalyst for the oxidation of the acceptor B if the oxidation potential of the reactants conformed to the scheme

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[1] *Proc. Roy Soc.* (*A*), 1924, **105**, **134**, **148**.

(*Fig* 14A) It is clear that the acceptor B can now reduce the oxidised inductor AO back to the original state A, in which it is capable of forming anew the unstable peroxide AO_2

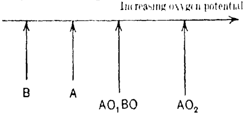


FIG 14A

This transition from a coupled to a catalytic oxidation process and vice versa, in agreement with the hypothesis of the order of the oxidation potentials outlined above, was examined for two particular cases

Salts of the colourless cerous oxide Ce_2O_3 are found to undergo coupled oxidation with arsenites in alkaline solution, but catalytically accelerate the oxidation of a number of sugars such as glucose, lactose, and fructose

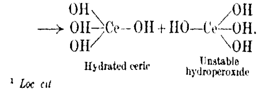
The oxidation potentials were found to be in the order

(i) Cerous salt (inductor), arsenite (acceptor), equilibrium mixture, perceric salt

(ii) Sugar (acceptor), cerous salt (inductor and catalyst), perceric salt

In the case of Schonbein s reaction, the separation of iodine from potassium iodide in the presence of ferrous salts and hydrogen peroxide, it was found that in neutral solution the oxidation potential of the inductor, the ferrous salt, lay far below that of the acceptor potassium iodide, and that the reaction was consequently coupled In acid solution, on the other hand, the relatively high oxidation potential of the inductor leads to its constant regeneration in presence of excess of the acceptor, so that the reaction becomes catalytic

The actual course of change in the case of cerous compounds acting as a part of a coupled reaction *e g* in the oxidation of arsenites, has been examined in detail by Job,[1] who has identified the existence of cerium salts in three states of oxidation - the colourless cerous salt corresponding to Ce_2O_3, the yellow ceric salt CeO_2, and a red peroxide He suggests the following mechanism of change



$$2\mathrm{Ce(OH)_3} + O_2 \longrightarrow \mathrm{(OH)_3Ce{-}O{-}O{-}Ce(OH)_3} + H_2O \longrightarrow \mathrm{(OH)_3Ce{-}OH} + \mathrm{HO{-}Ce(OH)_3}.$$

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[1] *Loc cit*

While the intermediate peroxide theory appears to be well substantiated, and the theoretical anticipations of the conditions of change from a coupled to a catalytic oxidation experimentally verified, there are nevertheless certain points which still await definite experimental verification.

We have noted that Moureu and his co-workers have come to the definite conclusion that the process of simple oxidation of a substance such as benzaldehyde proceeds through two steps, exemplified by the equations

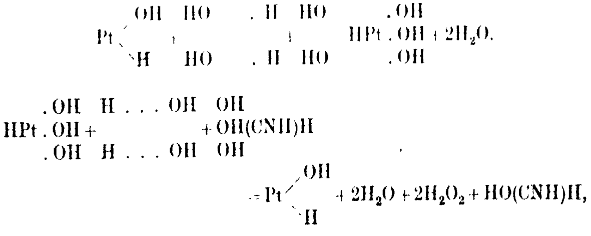
$$\begin{array}{ll}(1) & A + O_2 = AO_2. \\ (2) & AO_2 + A = 2AO.\end{array}$$

The question whether a reaction according to (2) actually takes place has not yet been definitely answered. As has already been indicated, Titoff's experiments on the oxidation of sulphites indicated the probability at least, if not the necessity, for a catalyst to be present. It would appear equally plausible to assume that the mechanism postulated by Moureu really involves two steps, in which a catalyst C plays a part:

$$\begin{array}{l}AO_2 + C = AO + CO. \\ CO + A = C + AO\end{array}$$

If positive catalysts are actually always required to cause the interaction of the unstable peroxide with the unoxidised substance so as to form an "electrical circuit", the many difficulties associated with the remarkable effects of small traces of inhibitors already referred to (pp 142-157) do not arise

The second point on which conclusive evidence is still lacking is how far the original hypothesis of the formation of an unstable peroxide by direct interaction of the substance with molecular oxygen is tenable Armstrong rejects the hypothesis, in that according to his view all these processes must be electrolytic in character Thus the inhibition by hydrogen cyanide of the decomposition of hydrogen peroxide by colloidal platinum is expressed as the formation of unstable "perhydrols" with their reversible interaction :



$$\mathrm{Pt}\begin{array}{l}\diagup OH \\ \diagdown H\end{array} + \begin{array}{l}HO \\ HO\end{array} + \begin{array}{l}.H\ \ HO \\ .H\ \ HO\end{array} = \mathrm{HPt}\begin{array}{l}.OH \\ .OH \\ .OH\end{array} + 2H_2O.$$

$$\mathrm{HPt}\begin{array}{l}.OH \\ .OH \\ .OH\end{array} + \begin{array}{l}H \ldots OH\ \ OH \\ H \ldots OH\ \ OH\end{array} + OH(CNH)H$$

$$= \mathrm{Pt}\begin{array}{l}\diagup OH \\ \diagdown H\end{array} + 2H_2O + 2H_2O_2 + HO(CNH)H,$$

and similar hydroxylations effected by the depolarising effect of oxygen on the elements of water acting as part of an electrical circuit must be imagined as the mechanism of formation of the peroxides required for these processes Some interesting peculiarities in oxidation catalysis are to be noted in the investigations of Rutter[1] on catalysis with vanadium salts Many examples of the effectiveness of these compounds as oxidation catalysts are to be found, such as the oxidation of sulphur dioxide, naphthalene, and benzene with air of aniline by chlorates, of mercury by bromates or hydrogen peroxide, and in the catalytic decomposition of hydrogen peroxide

The general method of representation of these catalytic changes may be written

$$MO_2 + V_{\text{lower}} \rightarrow MO + V_{\text{upper}}$$
$$V_{\text{upper}} + X \rightarrow XO + V_{\text{lower}}$$

The necessity for the oxidation potential of V_{upper} to be less than that of MO_2, but less than that of XO, has already been indicated if catalysis is to occur at all It is also clear that in addition the question of reaction velocity in the chemical reactions involved must be considered

Thus we find V^{III} can, like I^{I} and Fe^{II} ions reduce certain higher oxides V^{III} ions, however, reduce $HClO_3$ more rapidly than I^{I} or Fe^{II} ions, but reduce $H_2S_2O_8$ less rapidly than these ions

The interaction between $HClO_3$ and HI is relatively slow and is thus effectively catalysed by vanadium salts on account of the speed of the reactions $V^{III} + HClO_3$, $V^{IV} + HClO_3$ and $V^{V} + HI$ On the other hand, the reactions $FeSO_4 + H_2S_2O_8$ or $HI + H_2S_2O_8$ are scarcely affected by vanadium salts owing to the slow speed of the primary reaction $V^{\cdots} + H_2S_2O_8$ compared with that of the ferrous or iodine ion Rutter noted also that such catalytic oxidations might be attended with a primary coupled reaction, as in the following case

$$\underset{\text{Actor}}{\text{Chromic acid}} + \underset{\text{Acceptor}}{HI} + \underset{\text{Inductor}}{V^{III} \text{ or } V^{IV}} \rightarrow I_2 + V^{V} + \text{chromium salt}$$

The reaction proceeds in the following steps

$$CrO_3 + V^{III} \longrightarrow Cr_2O_5 + V^{V} \qquad Cr_2O_5 + I^{I} \longrightarrow Cr_2O_3 + I$$

Such reactions may be attended by periodic phenomena, as noted by Bray,[2] who found that under certain conditions the catalytic decomposition of hydrogen peroxides by iodates according to the reactions

$$5H_2O_2 + I_2 = 2HIO_3 + 4H_2O,$$
$$5H_2O_2 + 2HIO_3 = 5O_2 + I_2 + 6H_2O,$$

acquired a periodic character There is, however, a possibility that such periodicity may be due to inhomogeneity of the reacting solution

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[1] Dissertation, Berlin, 1906

[2] *J Amer Chem Soc*, 1921, 43, 1262

THE DRYING OF OILS

The use of siccatives to accelerate the drying of the oil in paints and varnishes is a very usual one, and has been the subject of much experimental investigation It has long been known that linseed oil, when exposed in thin films to the air, undergoes slow oxidation, a property used both in the paint and varnish industry as well as in the manufacture of linoleum

Lippert,[1] Weger,[2] and Kissling[3] showed that the "drying" was virtually a process of autoxidation, and that linseed oil could absorb or combine with more than 20 per cent of its weight of oxygen

The reaction velocity of this process of autoxidation was first examined by A Genthe,[4] who found that the increase of weight time curve exhibited the usual sinuous character of an autocatalytic reaction (Fig 15)

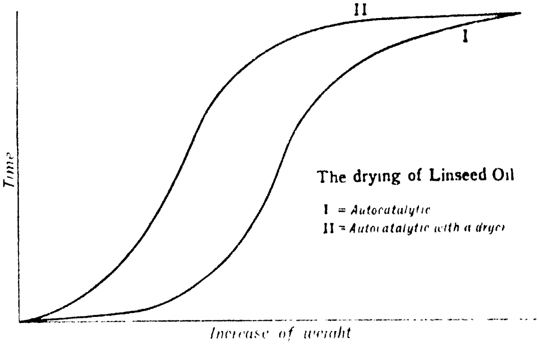

FIG. 15

It had therefore to be assumed that in the oxidation of linseed oil to linoxyn, a product, either an intermediary or the result of some side reaction, was formed, which exerted a catalytic function on the autoxidation of the oil

If a, b be the initial concentrations of linseed oil and autocatalyst respectively, then the rate of oxidation of the oil after a time t when x of the linseed oil has already been oxidised, is given by the equation

$$\frac{dx}{dt} = K(a - x)(b + x),$$

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[1] *Zeitsch angew. Chem*, 1898, **11**, 412.

[2] *Chem. Rev Fett-Harz-Ind*, 1899, **4**, 301.

[3] *Zeitsch. angew. Chem.*, 1891, **4**, 395

[4] *Ibid.*, 1906, **19**, 2087

an equation of the form corresponding with the curves obtained by Genthe in his experiments We must therefore postulate a quantitative relationship between the quantity of linseed oil oxidised and that of the autocatalyst simultaneously generated, a repetition of the phenomenon noticed in the autoxidation of the metals Experimental evidence also indicated that the autocatalyst was a peroxide, as is noticed in the autoxidation of turpentine, ether, and many other organic substances, thus Engler and Weiszberg,[1] who studied the effect of the addition of small quantities of turpentine on the reaction velocity, noticed that oil of turpentine which had been exposed to the air and contained more peroxide than fresh material exerted a superior catalytic activity Benzoyl peroxide and ether, which have been well shaken with air, likewise accelerated the reaction velocity In common with other autocatalytic processes which can be attributed to the formation of an unstable peroxide, light exerts a marked catalytic activity The oxidation also appears to proceed further under intense illumination than in the dark Genthe[2] found an increase of upwards of 34 per cent in weight during the oxidation of linseed oil when exposed to ultra-violet light

Linseed oil which has been boiled does not readily oxidise on exposure to the air, since the autocatalytic material originally present in the oil is destroyed by heat and the material itself has undergone polymerisation to less readily oxidised materials It regains some of its activity, however, on blowing with air

Although the mechanism of the process of drying is fairly clear from the above considerations, the actual chemical changes involved have by no means been elucidated Hazura,[3] Kissling,[4] Friend,[5] Baly,[6] Gardner,[7] King,[8] Salway,[9] and others have shown that several volatile products are evolved during the oxidation of the oil, including carbon dioxide and water vapour and certain toxic substances notably carbon monoxide and poisonous unsaturated aldehydes such as acrolein Linseed oil contains the glycerides as well as some of the free acid of a variety of organic acids, including linolenic, linoleic and oleic acids, as well as smaller quantities of mixed glycerides of stearic, palmitic, and other acids G Schicht[10] and Erdmann[11] considered linolenic acid to have the following structure

$$CH_3\ CH_2\ CH\ CH\ CH_2\ CH\ CH.CH_2\ CH\ CH(CH_2)_7\ CO_2H,$$

and linoleic acid,

$$CH_3\ CH_2\ CH\ CH\ CH_2.CH\ CH(CH_2)_{10}.CO_2H,$$

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[1] *Chem Zeit* 1903, **27**, 1196

[2] *Loc cit*

[3] *Zeitsch angew Chem*, 1888, **1**, 312

[4] *Ibid*, 1891, **4**, 395

[5] *Proc Paint Varnish Soc*, 1914, 140

[6] *J Soc Chem Ind*, 1912, **31**, 515

[7] *J Ind Eng Chem*, 1914, **6**, 91

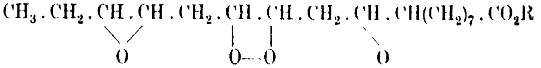
[8] *Ibid* 1915 **7** 302

[9] *J Chem Soc*, 1916, **109**, 138

[10] *Seifenfabrikant*, 1914, **34**, 13

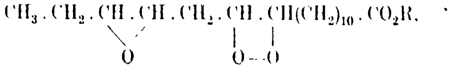
[11] *Ber*, 1909, **43**, 1324

the glycerides of which, according to Orloff,[1] undergo oxidation with the formation of peroxides, *e.g.*



$$CH_3.CH_2.\underset{\diagdown\,O\,\diagup}{CH.CH}.CH_2.\underset{O-O}{CH.CH}.CH_2.\underset{\diagdown O}{CH.CH}(CH_2)_7.CO_2R$$

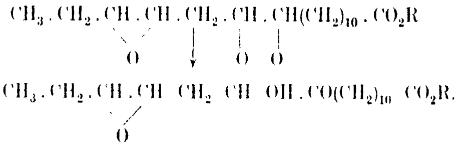
and



$$CH_3.CH_2.\underset{\diagdown\,O\,\diagup}{CH.CH}.CH_2.\underset{O-O}{CH.CH}(CH_2)_{10}.CO_2R.$$

R being the glycerine radical.

Fahrion[2] considered that the peroxide present in Orloff's oxidation products would be unstable and undergo intramolecular change to a ketoxy-group, forming, after condensation and elimination of water, the varnish-like stable solid linoxyn:

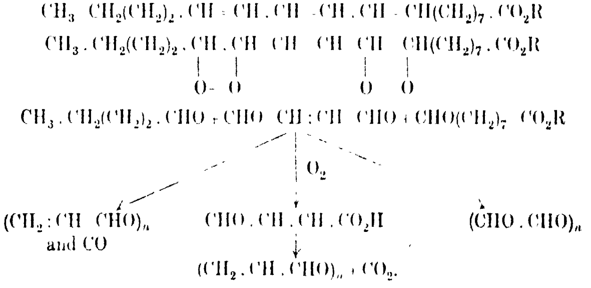


$$CH_3.CH_2.\underset{\diagdown\,O\,\diagup}{CH.CH}.CH_2.\underset{O\quad O}{CH.CH}(CH_2)_{10}.CO_2R$$

$$\downarrow$$

$$CH_3.CH_2.\underset{\diagdown\,O\,\diagup}{CH.CH}\ CH_2\ CH\ OH.CO(CH_2)_{10}\ CO_2R.$$

Salway, on the other hand, whilst postulating a different structure for linolenic acid from Erdmann, accounts for the formation of traces of aldehydes and carbon monoxide and dioxide during the process of autoxidation by postulating the intermediary formation of a dioxygenide.[3]



$$CH_3\ CH_2(CH_2)_2.CH:CH.CH:CH.CH:CH(CH_2)_7.CO_2R$$

$$CH_3.CH_2(CH_2)_2.\underset{O-O}{CH.CH}\ CH\ CH\ \underset{O\quad O}{CH\ CH}(CH_2)_7.CO_2R$$

$$CH_3.CH_2(CH_2)_2.CHO + CHO\ CH:CH\ CHO + CHO(CH_2)_7\ CO_2R$$

$$\xrightarrow{O_2}$$

$$(CH_2:CH\ CHO)_n \text{ and } CO \qquad CHO.CH.CH.CO_2H \qquad (CHO.CHO)_n$$

$$\downarrow$$

$$(CH_2.CH.CHO)_n + CO_2.$$

Linoxyn would thus be, substantially, a condensed aldehyde in unchanged linseed oil.

On the addition of very small quantities of siccatives such as the salts of manganese, lead, and, more rarely, cobalt, vanadium, and uranium, the drying process is considerably shortened and the S-shaped curve follows that indicated by II.[1]

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[1] *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 658.

[2] *Zeitsch. angew. Chem.*, 1910, **23**, 723.

[3] See Salway and Kipping, *J. Chem. Soc.*, 1909, **95**, 166.

It is still a matter of dispute whether the siccative is a catalyst *per se* for the oxidation of linseed oil, or whether it catalytically hastens the formation or stabilises the presence of the autocatalytic peroxide and thus exerts a pseudo-catalytic function.

If initially present in very large quantities the quantity of autocatalyst may be neglected and the form of the curve would be represented by the simple equation

$$\frac{dx}{dt} = k'(a - x)$$

Some experiments, however, by Rideal point to the persistence of the "period of induction", followed by a rapid rise in the value of dx/dx, we must therefore assume that the siccative is pseudo-catalytic in behaviour and serves either to stabilise or assist in the formation of the autocatalytic peroxide.

The metallic salts of weak acids are usually employed, *e.g.* the borates. These, however, suffer from the disadvantage of being insoluble in the oil. Under these conditions the influence of the siccative present as a heterogeneous phase in the oil is not very marked, and, at the same time, the small solid particles present in the oil, even when they are chemically inert as, for example, in the case of silica or barytes, act as negative catalysts,[2] since they assist in the decomposition of the autocatalytic peroxides. For this reason soluble organic salts, usually the soaps, are generally employed. Lead oleate, cobalt linoleate, and manganese rosinate are examples of such soaps.

Ingle,[3] and Mackey and Ingle,[4] as a result of a long series of investigations on the action of siccatives, arrived at the following conclusions:

(1) In its oil soluble form, *i.e.* as a soluble metallic soap, those metals which exist in more than one state of oxidation act as driers, provided that the salts of the lower oxides are more stable than those of the higher oxides.

(2) Metals which form a number of oxides are more active than the mono- or divalent metals.

The results obtained in the investigations of Ingle are summarised in the following table (Fig. 16). The black lines indicate the time required for 7 grms. of cotton-wool, oiled with 14 grms. of linseed oil (iodine value 178), and mixed with 2 per cent of metallic soap, to attain a temperature of 200° in a cloth oil-tester. The shaded lines give the corresponding times required for 14 grms. of olive oil (iodine value 55) to attain the same temperature under similar conditions.

Copper proved to be somewhat erratic in behaviour, acting first as an accelerator and subsequently inhibiting the oxidation. It was shown that this action was due to the precipitation of cuprous oxide in the oil on elevation of the temperature.

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[1] See p. 221, *ante*.

[2] Gardner, *J. Ind. Eng. Chem.*, 1914, **6**, 91.

[3] *J. Soc. Chem. Ind.*, 1916, **35**, 454.

[4] *Ibid.*, 1917, **36**, 317.

It will be noted that both sodium and silver show catalytic activities which are considerably higher than would be expected from Mackey and Ingle's generalisations, and for which no explanation is as yet forthcoming.

Further investigation on the influence of H' and OH' on the reaction velocity may indicate that the optimum conditions are to be found when the oil, which always contains small quantities of water

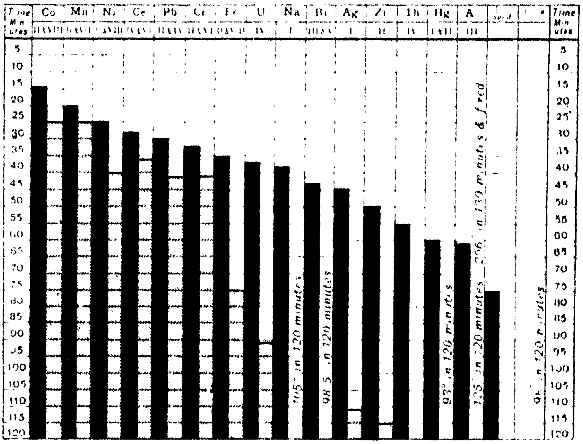


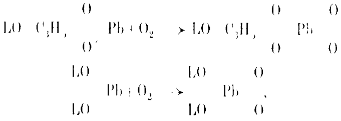
FIG. 16.

resulting from the autoxidation, is slightly alkaline, the sodium soap serving to neutralise the small quantities of relatively strong acids, such as acetic and formic acid, which are by-products of the oxidation. In the case of the silver soap, the precipitation of colloidal silver, especially since Cu_2O has been shown to be formed above 100°, may be expected, and this would probably show enhanced activity as an oxygen carrier.

Ingle attributes the action of siccatives to the intermediary formation of peroxides. Thus, on the addition of litharge to linseed oil partial saponification of the glyceryl linolenate results in the formation of lead linolenate and glyceryl plumbo-linolenate :

$$C_3H_5(OL)_3 + 2PbO \longrightarrow PbO_2 . C_3H_5OL + Pb(OL)_2.$$

Both these lead salts can form compounds with atmospheric oxygen to give compounds of tetravalent lead

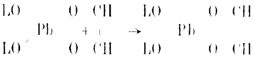


$$\begin{matrix} & \mathrm{O} & & & & \mathrm{O} & & \mathrm{O}\\ \mathrm{LO\ \ C_3H_5} & & \mathrm{Pb} + \mathrm{O_2} & \rightarrow & \mathrm{LO\ \ C_3H_5} & & \mathrm{Pb} & \\ & \mathrm{O} & & & & \mathrm{O} & & \mathrm{O}\end{matrix}$$

$$\begin{matrix}\mathrm{LO} & & & \mathrm{LO} & & \mathrm{O}\\ & \mathrm{Pb} + \mathrm{O_2} & \rightarrow & & \mathrm{Pb} & ,\\ \mathrm{LO} & & & \mathrm{LO} & & \mathrm{O}\end{matrix}$$

in which L denotes the linolenic acid radical

Further reaction may then occur with the unsaturated double linkages of the fatty acids and glycerides present in the oil



$$\begin{matrix}\mathrm{LO} & & \mathrm{O\ \ CH} & & \mathrm{LO} & & \mathrm{O\ \ CH}\\ & \mathrm{Pb} & + & \rightarrow & & \mathrm{Pb} & \\ \mathrm{LO} & & \mathrm{O\ \ CH} & & \mathrm{LO} & & \mathrm{O\ \ CH}\end{matrix}$$

and thus hasten the normal oxidation velocity of the oil

CHAPTER VIII

HYDROGEN AND HYDROGENATION

THE MANUFACTURE OF HYDROGEN

THE increasing employment of hydrogen in modern technical processes, as for example, in the hydrogenation of oils and the fixation of atmospheric nitrogen as ammonia has created the problem of a cheap hydrogen supply. Moreover, the demand in catalytic hydrogenation processes for purity of materials necessitates in many cases the production of hydrogen in a high degree of purity.

The sources of hydrogen supply are various. Electrolytic hydrogen, naturally, can be readily obtained with the necessary degree of purity, but the cost factor in the majority of circumstances renders its use prohibitive. By another method, in use on a large technical scale, hydrogen is produced by the decomposition of steam in presence of heated iron, the resulting oxide of iron being reduced to the metallic condition by means of water gas. With careful regulation this process may be made to yield hydrogen of the requisite purity. Without due attention, however, the presence of prohibitive concentrations of carbon monoxide in the gas, resulting from the action of steam on carbon deposited in the iron from the water gas during the reducing phase, may render the hydrogen unsuitable for use in certain catalytic operations. Furthermore, the economy of the process is, at present, low, and the cost factor, therefore, somewhat high.

The analogous process of Bergius, already investigated upon a small technical scale, generates hydrogen under high pressure and with great purity, by the action of liquid water upon finely divided iron at moderate temperatures in closed steel bombs. The pressures employed are generated by the reaction itself and are sufficient to maintain the water in the liquid state. The temperatures required, apart from the initial heat necessary to start the reaction, are maintained by the exothermicity of the reaction. Like the previous method of preparation, the process is discontinuous, the oxide of iron produced simultaneously with the hydrogen requiring subsequent reduction to the metallic state.

Hydrogen may also be produced from water gas by liquefaction of the carbon monoxide at the temperatures of liquid air boiling under reduced pressures. By this method complete separation of the constituents of the water gas is not readily attainable and, in common practice, a hydrogen containing from 2 to 3 per cent of carbon monoxide is generally obtained. A more complete separation of the two gases may only be obtained with a prohibitive decrease in the yield of hydrogen, since a mixture of hydrogen with 2 per cent of carbon monoxide behaves almost exactly like hydrogen in its physical properties. Actually, the yield of hydrogen would be considerably increased if a 95 per cent hydrogen were obtained by the liquefaction process, the remaining 5 per cent of carbon monoxide being subsequently removed by other means.

The water-gas catalytic process.—The most recent technical method for the production of hydrogen, and in many ways the most promising as regards cheapness of production, involves a catalytic operation using water gas and steam as the reaction materials. In the presence of suitable catalytic agents, at regulated temperatures, carbon monoxide and steam react to yield carbon dioxide and hydrogen. Utilising water gas, therefore, a gas rich in hydrogen would result, the problem of further purification involving the removal of the carbon dioxide formed and of the unconverted carbon monoxide.

The reaction occurring, which may be formulated by means of the equation

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

is in reality an equilibrium process, the direction of the reaction being governed by the temperatures maintained and the concentrations of the respective components. The equilibria obtaining at various temperatures may, in the absence of experimental data over the whole range of temperatures required, be calculated from the experimental work of Hahn[1] at higher temperatures. In this way the following approximate values for the equilibrium constant

$$K = \frac{p_{H_2O} \times p_{CO}}{p_{H_2} \times p_{CO_2}}$$

at the various temperatures are obtained:

T	400	500	600	700	800
K	0.05	0.1	0.3	0.6	0.9

From these figures it is obvious that high temperatures favour th production of carbon monoxide in agreement with experience in water gas manufacture. Lower temperatures favour the production o carbon dioxide and hydrogen. The lower the temperature at whic the water-gas reaction occurs, the greater will be the conversion o carbon monoxide to dioxide with the corresponding increase in yiel and purity of hydrogen. On the other hand, decrease of temperature slows down the reaction velocity, so that, in practice, a low limit to the temperature will be set below which attainment of equilibrium conditions requires the presence of catalytic agents. It is obvious from these facts that, for the successful production of hydrogen from water gas, catalytic agents are required which will rapidly promote the reaction at as low a temperature as possible.

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[1] See Haber, *Thermodynamics of Technical Gas Reactions*.

A considerable patent literature relative to this process already exists. The basic patent for the production of hydrogen from gases containing the same in admixture with carbon monoxide and hydrocarbons was granted to Mond and Langer.[1] According to this invention, the gases were to be passed with excess of steam over heated catalysts, for example, nickel at temperatures of 350-400°, cobalt at 400-450°. The hydrocarbons were said to be decomposed, while the carbon monoxide was converted to the dioxide, which was thereupon removed. It was subsequently claimed that the gas produced was almost free from carbon monoxide. Elworthy suggested the employment of nickel or iron in a similar manner with a mixture of water gas and steam. A patent of Pullman and Elworthy[2] proposes to separate the carbon dioxide and hydrogen by processes of diffusion and of fractional solution. In 1907 Vignon applied for a patent[3] for a process as above, using iron or oxides or platinum at red heat. The patent was not granted. Ellis and Eldred[4] employed nickel, iron, or manganese for catalytic agents of the water gas steam reaction, using a specially designed superheated reaction chamber. Naher and Muller[5] suggest the use of a contact mass of rhodium or palladium asbestos at a working temperature of 800. They claim a product with less than 0·4 per cent of carbon monoxide. It is obvious that at a temperature of 800 such a low content of carbon monoxide can only be obtained by the use of large excesses of steam, which would render the process economically impossible. More recently a considerable number of patents have been obtained by the Badische Anilin- und Soda Fabrik relative to the process, which has been established by them on a commercial basis. B.P. 26770/1912 calls for the carrying out of the process under pressures of 4-10 atmospheres at temperatures between the limits of 300° and 600°, using nickel and cobalt as catalysts. The increase in pressure improves both the reaction velocity and the heat regeneration. So conducted it was claimed to be specially useful for gases with small carbon monoxide content. Later, in 1912,[6] an improvement was patented for the maintenance of the requisite temperature in the catalytic mass by the addition of air or oxygen, which, combining with some of the hydrogen, generated sufficient heat to enable the process to be maintained continuously, especially if only small amounts of carbon monoxide were present. A patent of 1913[7] by the same company deals with suitable catalysts, the basis of which was oxide of iron with suitable binding agents. B.P. 8864/1913 is concerned with catalysts containing nickel, cobalt, and similar substances, which apparently tend towards the simultaneous production of methane, since B.P. 27963/1913 deals with catalysts which do not produce methane by side reaction. The materials here cited as catalysts are numerous and involve as basic substance principally iron oxide in admixture with one or more substances acting as promoters of the activity of the iron oxide. Chromium, nickel, aluminium, thorium, zinc, lead, uranium, and other oxides are cited in this connection. A later patent[1] returns to the claims of B.P. 27955/1913, amplifying them by claiming, for use as catalysts, oxide, hydroxide, and carbonaceous iron ores employed either in bulk or brought into suitable form by powdering and admixture with binding agents. The minerals employed should preferably be free from sulphur, chlorine, phosphorus, and silicon, though small amounts of these are said to be permissible. It is insisted, with regard to the production of all these catalysts, that high temperatures should be avoided in the course of preparation, and a limit is set at preferably below 650°. It is obvious that such limitations exclude from use the oxide of iron obtained by the roasting of pyrites ores. The utilisation of this material for catalytic preparations is the subject of a patent by Buchanan and Maxted,[2] who claim the use of the oxide of iron obtained from sodium ferrite as catalyst. The material is prepared by fusion of burnt pyrites with sodium carbonate at elevated temperatures, followed by lixiviation of the mass thus obtained. The mass of iron oxide so prepared, and containing some undecomposed ferrite, is claimed to give good conversion at moderate temperatures. A succeeding patent of Buchanan and Maxted[3] claims the use of metallic couples as improved catalysts. Thus, by reduction of the iron oxide obtained in the manner cited in the previous patent and by immersion of the iron thus produced in a solution of copper salts, a metallic iron-copper couple is obtained with which improved conversion at increased velocities is claimed.

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[1] B.P. 12608/1888.
[2] B.P. 22340/1891.
[3] B.P. 20685/1907.
[4] U.S.P. 854157/1907.
[5] B.P. 20486/1911.
[6] B.P. 27117.
[7] B.P. 27955.

The actual material used in technical operation will depend not only on catalytic activity but also on factors such as robustness of catalytic material and durability towards impurities in the raw materials used for manufacture. Oxides of iron, either from minerals such as spathic ore, or prepared from iron compounds, are the main constituents of technical catalysts. Promoters such as chromium and cerium oxides improve the oxides of iron markedly. The technical details of the process need not be given here, since they have been fully treated in a number of publications.[4]

Assuming a working temperature of 500° and a catalytic agent capable of producing equilibrium at rapid gas velocities it is interesting to note the products to be obtained from a commercial blue water gas containing, say, 40 per cent of carbon monoxide. At 500

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[1] B.P. 16494/1914. [2] B.P. 6476/1914. [3] B.P. 6477/1914.

[4] See, for example, Taylor, *Industrial Hydrogen*, chap. iii (Chemical Catalog Co., New York, 1922).

$$k = \frac{p_{H_2O} \times p_{CO}}{p_{H_2} \times p_{CO_2}}$$

is approximately equal to 0·1, so that with equal concentrations of steam and hydrogen in the exit gases it is obvious that $p_{CO} : p_{CO_2} = 0·1$, that is, there would be approximately 4 per cent of carbon monoxide in the residual products when the steam was eliminated. In practice it is customary to reduce this percentage by employing excess of steam, the amount of reduction being governed by the amount of steam used. Apparently the best economic balance is secured by employing sufficient steam to reduce the carbon monoxide content of the residual gas to 2 per cent. This involves, according to the equilibrium data, a steam : hydrogen ratio in the exit gases of 2 : 1 or an initial ratio of water gas to steam of 1 vol. water gas to $2\frac{1}{2}$ vols. of steam, according to the equation

$$\underbrace{H_2 + CO}_{\text{Water gas}} + 5H_2O \rightleftarrows 2H_2 + CO_2 + 4H_2O$$

Using these approximate quantities, a typical analysis of the resulting gas will be somewhat of the order H_2 65 per cent, CO_2 30 per cent, CO 2 per cent, N_2, etc. 3 per cent.

The thermal balance of the process may now be considered. The reaction occurring

$$CO + H_2O \rightarrow CO_2 + H_2$$

is exothermic, 10,000 cals. being liberated per molecule of carbon monoxide converted. With good heat exchangers capable of yielding a 75 per cent heat regeneration, the evolution of heat is sufficient to cover all conduction and radiation losses. Only at starting is preheating requisite, for which purpose water gas may be burnt. Subsequently the mixed water gas and steam pass through heat exchangers in which they are brought to the reaction temperature of about 500 by means of the heat of the exit gases passing in the reverse direction and leaving the heat exchangers at a temperature of approximately 100. With such a procedure the process is continuous, a factor of considerable advantage as compared with other processes of hydrogen production.

The economy of the process may be illustrated from another point of view. Consideration of the reaction equation will show that, theoretically, for the production of 1 volume of hydrogen, 1 volume of water gas is required. In practice it is claimed that 1·1 volumes of water gas are sufficient. This is in marked contrast to the conditions obtaining in the steam-iron process, in which from 2 to 4 volumes of water gas are required, according to practical experience, for the production of 1 volume of hydrogen. As regards the economy of steam in the process, it must also be observed that although an excess of steam is required in this process to decrease the final carbon monoxide content, the steam consumption is much less than in the intermittent steam-iron process, in which, as at present employed, as much as three or four times the theoretical amount of steam required is employed for the production of unit volume of hydrogen

A further advantage of the process exists in that crude water gas may be employed, no special purification other than the removal of mechanical impurities, such as flue dust, being required This economy is realisable owing to the fact that all the organic sulphur compounds present in the gas are converted catalytically into sulphuretted hydrogen This process of sulphur conversion is interesting in other connections and is dealt with in more detail elsewhere in this book The sulphuretted hydrogen formed in this manner, together with that originally present in the gas, can readily be removed from the resulting gas mixture along with the carbon dioxide Obviously therefore, the hydrogen obtained, being sulphur free, is especially suitable for certain catalytic operations as, for example ammonia synthesis

The disadvantages associated with the catalytic process may be enumerated In the first place, there is the removal of the carbon dioxide, which forms upwards of 30 per cent of the exit gases from the condensers Actually this is carried out in practice by a system of counter current water-washing under pressures of about 30 atmospheres The system is well tried and yields hydrogen with a carbon dioxide content of less than 1 per cent which residue may be subsequently removed by lime or alkalis If the hydrogen has afterwards to be used in the compressed state, the compression costs are negligible Large quantities of water must necessarily be conveniently to hand however, for the operation of the process Part of the energy necessary for pumping the water is recoverable by making the issuing water work an appropriate motor By means of a Pelton wheel arrangement 30 to 50 per cent of the energy may be recovered Simultaneously with the carbon dioxide sulphuretted hydrogen is also removed A certain loss of hydrogen occurs during the process of water-washing, presumably of the order of 10 per cent

The removal of the unconverted carbon monoxide forms a second obstacle to the utilisation of the catalytic process Numerous methods have been suggested for effecting this Certain processes involve methods of absorption, for example, by ammoniacal cuprous salts under pressure The conversion of carbon monoxide to sodium formate by hot caustic-soda solutions under pressure has also been utilised for removal The gases when freed from carbon dioxide and sulphur compounds are also sufficiently pure to enable one to remove the carbon monoxide by conversion at the expense of hydrogen to methane, using a nickel catalyst The Badische patent[1] previously cited reduces the monoxide content of the gas by repetition of the main catalytic process under pressures of 4-40 atmospheres. Preferential combustion of the carbon monoxide in the hydrogen has been proposed by Harger and Terry[1] and applied to the particular product from the water-gas catalytic process by Rideal and Taylor[2] with a high-temperature (200° C.) catalyst of iron-chromium-cerium oxides, and by Lamb, Scalione, and Edgar[3] with a catalyst consisting of copper and manganese oxides at temperatures below 100° C. It is obvious that the particular process adopted may be governed by various factors operating to determine the choice.[4]

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[1] B P 26770 1912

For certain purposes a further disadvantage of the catalytic process lies in the presence in the final hydrogen of the inert gases, *e.g.* nitrogen, methane, etc., present in the original water gas. For ammonia synthesis the presence of nitrogen is no disadvantage. In other catalytic operations it may act as a diluent, and in circulating systems tends—as does methane also—to accumulate in the gaseous system and so finally bring about a stoppage in the process for the rejection of the diluted hydrogen, or a constant loss of spent gas by continuous removal from the circulatory system.

In spite of these disadvantages it would seem that the continuous catalytic process is the cheapest and most promising of the processes for large-scale hydrogen production. It is a process also which still offers considerable possibilities for development and improvement, mainly in the treatment of the gases obtained from the contact mass. The efficiency of the process up to this stage may be regarded as already very high.

The problem of removal of the large quantities of carbon dioxide obtained by catalytic conversion of water gas and steam is the object of another series of patented processes employed upon a technical scale by the Griesheim Elektron Co.[5] The catalytic material is lime suitably activated by admixture of substances like oxide of iron. Operating at temperatures of 400-500°, conversion to carbon dioxide and hydrogen of the water gas and steam is readily attained. The lime at these temperatures absorbs the carbon dioxide, yielding carbonate, since only above 600° does the dissociation pressure of calcium carbonate become marked.[6] Absorption of the carbon dioxide disturbs the equilibrium which otherwise would prevail, and so the carbon monoxide is thereby more completely removed. Also, the resulting gas does not contain the large quantities of carbon dioxide obtained in the process previously considered. On the other hand, it is obvious that owing to the conversion of the lime into carbonate the process is necessarily discontinuous, the lime requiring regeneration by heating to more elevated temperatures. The employment or rejection, therefore, of such a process as an alternative to the catalytic process previously considered hinges on the economy of the regeneration of the lime catalyst as against the process of water-washing under pressure. It will be obvious that for a large-scale hydrogen plant the lime required will be enormous, of the order of 100 lbs. of lime for 1000 cubic feet of water gas containing 15 per cent. of carbon monoxide, assuming that as much as half the lime may be converted to carbonate without impairing its ability to remove the carbon dioxide from the gases produced. It is doubtful whether the expense of regeneration of such quantities of lime would compete in a large technical unit with the continuous system of removal of carbon dioxide by counter-current water-washing. Disintegration of the lime during the process also forms a further disadvantage in practical operation.

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[1] B.P. 127,609/1917.

[2] *Analyst*, 1919, **44**, 89.

[3] *J. Amer. Chem. Soc.*, 1922, **44**, 738.

[4] For a complete treatment of the industrial problems in the manufacture of hydrogen by the various processes, see Taylor, *Industrial Hydrogen*, A.C.S. Monograph (Chemical Catalog Co., New York, 1921).

[5] B.P. 2523/1909.

[6] Johnston, *J. Amer. Chem. Soc.*, 1912, **32**, 946.

The original patents for the lime process were due to Tessié du Motay (1880). The improvement of the Griesheim Elektron Co., which consisted in the addition of 5 per cent. of iron powder to act as an accelerator, was studied theoretically by Engels,[1] who found that equilibrium conditions could be obtained at markedly increased velocities of passage of the steam-water gas mixture when such activators were present. It is obvious that the addition of the iron tends to promote the water gas reaction as in the continuous catalytic process detailed above, and, therefore, also promotes the attainment of equilibrium with the lime. Doubtless, too, it would be found that the active catalysts (iron oxide with promoters) of the continuous process would also accelerate considerably the lime process. Further, a method of procedure should be possible in which the steam-water gas mixture passed first at 400°-500° over an efficient catalyst for the water gas reaction, then over lime in a second chamber maintained at the same temperature to remove the carbon dioxide, and finally over a further mass of the original catalytic material in which the residual carbon monoxide should be further converted by steam to carbon dioxide, leaving only minimal quantities of carbon monoxide in the hydrogen obtained.

According to Mertz and Weith,[2] carbon monoxide and steam react when passed over soda lime at temperatures of 300° and upwards. This method of manufacture of hydrogen has been suggested for technical operation by the Société générale des Nitrures of Paris[3] and the Chemische Fabrik Griesheim Elektron.[4] R. E. Wilson, Hasslacher and Masterson[5] have studied the reaction in somewhat greater detail and conclude that soda-limes with high caustic-soda content are better than those with low, or than lime alone. The former give substantially complete removal of 2 per cent. carbon monoxide in hydrogen mixtures at around 400° C. Small amounts of water vapour are helpful, though not essential, to the efficiency. These authors claim that the fundamental reaction for the removal of the gas at the higher temperatures is

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[1] Dissertation Karlsruhe, 1911. *Chem. Abs.* 1920, **14**, [illegible].

[2] *Ber.*, 1880, **13**, 719.

[3] D.R.P. 248290.

[4] B.P. 13049, 1912.

[5] *J. Ind. Eng. Chem.* 1923, **15**, 698.

$$CO + 2NaOH = Na_2CO_3 + H_2.$$

An alternative series of processes for the production of hydrogen-carbon dioxide mixtures from steam and coke are embodied in the patent claims of Dieffenbach and Moldenhauer. Instead of employing catalytic agents to bring about the water gas reaction, these claimants propose to facilitate, by addition of catalysts, the reaction between coke and steam, so that it may be carried out at such low temperatures that the products of interaction are principally carbon dioxide and hydrogen. In B.P. 7719/1910 the addition of an alkaline hydroxide or salt, and especially a silicate, is suggested to enable the reaction between coke and steam to be effected within the temperature interval 550°-750°. In B.P. 7720/1910 the use of alkalis and alkali salts is suggested. The use of both alkali and lime, it is stated,[1] still further decreases the temperature at which steam and coke will react with rapidity. Neville and Taylor [2] have made a theoretical study of these patents and find that the alkali carbonates alone operate as really efficient catalysts. They showed that the catalysis involved an acceleration of the reaction between carbon dioxide and carbon rather than the effect of the catalyst on the water gas reaction,

$$CO + H_2O = CO_2 + H_2.$$

It was shown that the absorptive capacity for carbon dioxide of a charcoal containing such catalysts was markedly greater than that of the same charcoal in the absence of such agents.

The steam-iron process of hydrogen manufacture. As outlined in the introductory paragraphs of this chapter, the production of hydrogen by the action of steam on heated iron is already largely carried out in the industry. The main reaction which occurs may be represented by the equation

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

By reduction, usually with water gas, of the oxide of iron thus obtained the iron may be regenerated and the cycle of operations repeated.

The original patents for the process are very old; thus, for example, in B.P. 593/1861 Joseph Jacob claims the commercial production of hydrogen by the action of steam on iron filings or borings, or on iron crushed, ground, or pulverised. The heat of the retorts was to be maintained by combustion of a portion of the hydrogen produced; the iron after oxidation was to be discharged from the retort.

The alternate reduction and steaming process was patented by Lewes.[3] Hills and Lane [4] and Hills and Monteux [5] utilise this principle in specially designed apparatus for commercial production The earlier types of plant have been considerably modified in detail as a result of accumulated experience, but the principle of operation remains substantially the same Further economies of operation are claimed in the numerous patented details of Messerschmidt [1]

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[1] B.P. 8734/1910.

[2] *J. Amer. Chem. Soc.*, 1921, **43**, 2055.

[3] B.P. 20752/1890 and B.P. 4134/1891.

[4] B.P. 10356/1903.

[5] F.P. 386991/1908.

According to the patent specification of Lewes, iron borings may be employed for the reaction Since the two phases of the process are, however, *mainly surface actions, or at most penetrate* but little into the interior of the material, *recent* practice has resolved itself into the substitution, for metallic iron, of iron in a porous or spongy condition which will offer a maximum of surface for a minimum of volume The iron is therefore generally obtained by reduction of a mineral oxide or from carbonate ores such as spathic iron ore by reduction of the mass obtained after ignition and loss of carbon dioxide In this way material possessing both porosity and resistance to disintegration is readily obtained Roasted pyrites from which all sulphur and the volatile metals have been removed has also been proposed as the reaction material [2] All such materials show a greater or less tendency to lose their activity with repeated oxidation and reduction, and research into the causes thereof conducted on the large technical scale has shown it to be in part due to fritting of the surface Part of the loss in activity is due to deposition of foreign bodies such as carbon, sulphur, etc, in the mass, but these may be removed by periodical heating in a current of air The fritting however is permanent, and consequently many suggestions have been put forward to counteract this difficulty They consist chiefly in the admixture with the iron of bodies which may either render the iron less fusible and less liable to soften with the temperatures employed, or which may catalytically assist the interaction of steam with iron so that good yields of gas may be obtained at lower temperatures than would normally prevail Thus, Messerschmidt proposes [3] the use of natural ores of manganese and of manganese and iron to attain lower reaction temperatures Dieffenbach and Moldenhauer [4] claim the use of alloys of iron with manganese, chromium, tungsten, titanium, aluminium or other similar elements, as well as mixtures of the oxides briquetted or in other suitable form The Badische Anilin- und Soda Fabrik [5] propose iron oxide fused with refractory oxides such as zirconia and magnesia or with silicates Jaubert [6] suggests the use of briquettes of iron oxide admixed with fire-clay, pumice, magnesia, and small amounts of the oxides of manganese, chromium, copper, and lead

The gas obtained by the steam-iron process contains, after removal of small quantities of carbon dioxide and hydrogen sulphide by means of lime purifiers, upwards of 98 per cent of hydrogen With careful control a content of hydrogen as high as 99·75 can be continuously maintained without considerable increase in cost of production. Higher purity still, averaging 99·85-99·95 per cent of hydrogen, can be maintained by extraordinary precautions as to scavenging and by use of an elevated temperature coupled with frequent aeration of the contact mass. Naturally this increases considerably the cost of the gas owing to loss of yield, decreased activity of the iron due to fritting, and wear and tear of retorts at the high temperatures.

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[1] See *J Soc Chem Ind*, 1914 **33** 313, also Taylor *Industrial Hydrogen, loc cit*

[2] B P 7849 1909

[3] F P 461480 1913

[4] D R P 233347 1910

[5] F P 440780 1912

[6] F P 418312 1909

The main impurity of the gas is carbon monoxide resulting from interaction of the steam and carbon deposited in the iron during the reducing phase. This carbon results from the catalytic decomposition of the carbon monoxide[1] in the presence of iron, according to the equation

$$2CO \rightleftarrows C + CO_2.$$

In the steaming phase this carbon reacts with the steam to form carbon monoxide and dioxide, the concentration of steam present determining to a considerable degree the relative quantities of each in the issuing gas. As stated, the carbon dioxide is removed by means of lime purifiers or caustic-soda liquor, the carbon monoxide passing on with the hydrogen. Since the carbon in the iron mass is only incompletely decomposed by the steam it gradually accumulates in the material and must therefore be occasionally removed by means of a hot air current.

The Bergius hydrogen process.—The patents of Bergius[2] relative to the manufacture of hydrogen by the action of liquid water, at elevated temperatures and therefore at high pressures, upon carbon or iron disclose certain interesting details as to the use of catalytic accelerators.

Bergius found that, at a temperature of 300° and at a pressure sufficient to keep the water liquid, carbon reacted almost exclusively with water to form a mixture of carbon dioxide and hydrogen, according to the equation

$$C + 2H_2O \longrightarrow CO_2 + 2H_2$$

The addition to the water of small quantities of thallium salts was found to promote the reaction catalytically.

Employing iron, the corresponding reaction with liquid water also took place at the low temperature of 300°. Only in the initial stages of the reaction was heat required, the exothermicity of the reaction being sufficient to maintain the gas evolution. Pressures of 100 atmospheres or more were generated in the system and were reduced to the desired extent by occasionally blowing off the gas through a valve into cylinders in which the hydrogen could be stored already compressed. Catalytic acceleration of the reaction was secured by dissolving in the water neutral salts, as, for example, sodium chloride or acids, or by use of metallic couples such as iron-copper, or by the presence of a second metal such as nickel or platinum.

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[1] For equilibria, see Boudouard, *Compt. rend.*, 1900, **130**, 132; Rhead and Wheeler, *J. Chem. Soc.*, 1912, **101**, 831.

[2] D.R.P. 259030/1911, 254593/1911, and 262831/1912.

The Bergius iron-water process should be cheap and useful for small-scale hydrogen production under pressure where an expensive equipment is not possible. Regeneration of the finely divided iron metal employed can be effected by means of water gas, producer gas, or carbon at high temperatures.

Hydrogen production by catalytic decomposition of hydrocarbons. – In general, the saturated hydrocarbons when subjected to a sufficiently high temperature decompose into their elements, the carbon being deposited in an extremely fine state of division, hydrogen being simultaneously produced.[1] The temperature required for decomposition varies with the stability of the compound. Thus, methane dissociates rapidly only at 1200° to 1300°, its presence in a water gas mixture being evidence that at the slightly lower temperature of water gas manufacture the velocity of decomposition is comparatively low. On the other hand, acetylene decomposes at much lower temperatures, Pictet[2] effecting decomposition by passage through tubes heated initially to 500°. Since heat is evolved upon the decomposition of acetylene, the reaction continues automatically when once started. This process is generally applicable to endothermic hydrocarbons.

Numerous patented processes exist for the production of hydrogen by this method, the variations being, in the main, modifications for the better operation in technical practice. Thus the Carbonium Co., of Friedrichshaven, have decomposed acetylene under pressure by explosion with an electric spark. The hydrogen obtained is of high purity and has been employed for the filling of Zeppelins. The cost is, however, somewhat considerable unless the lamp-black can be marketed. The pressures employed may be as much as 6 atmospheres.[3]

The decomposition of the light petroleum hydrocarbons is the subject of patents by Lessing[4] and by Pictet[5] in which temperatures from 1000°–1350° are suggested. It is obvious that technical operation at such high heats is a matter of considerable difficulty, and it is not surprising that extended application has not yet been recorded. Recent work on the cracking of heavier hydrocarbon vapours will doubtless contribute greatly to the development of technique in this direction.

To bring about the decomposition of hydrocarbons at lower temperatures interaction with steam has been employed both with and without catalytic contact material. Pictet[6] produces thus carbon monoxide and hydrogen from hydrocarbon vapours and steam at high temperatures. The Badische Anilin- und Soda-Fabrik[7] suggest a refractory oxide such as magnesia impregnated with nickel oxide as catalyst for this process, at a temperature of 800°. Dieffenbach and Moldenhauer[1] use as catalyst wire gauze of nickel, cobalt, platinum, etc., for the same reaction, ensuring by the employment of the catalyst in such form a very short time of contact and thereby a sudden cooling of the reaction products. In this way, it is claimed, the carbon dioxide formed has little opportunity to be reduced to carbon monoxide. An important study of the many reactions involving the methane equilibrium, for example,

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[1] Meyer and Altmayer, *Ber.*, 1907, **40**, 2134.

[2] F.P. 421849/1910.

[3] Machtolf, D.R.P. 194301/1909.

[4] B.P. 15071/1909.

[5] B.P. 13397/1911.

[6] B.P. 14703/1911.

[7] B.P. 12978/1913.

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2,$$
$$CH_4 + H_2O \rightleftharpoons CO + 3H_2,$$

has recently been completed.[2] This should prove useful in the theoretical study of this important technical problem.

Coke rendered white hot by an air blast has been proposed by the Berlin Anhaltische Maschinenbau A.G.[3] and by Ellis[4] as contact material for the production of hydrogen from paraffin hydrocarbons.

It should be possible with the aid of catalytic contact material to bring about the interaction of hydrocarbons with carbon dioxide to yield carbon monoxide and hydrogen, whence pure hydrogen could be obtained by processes described above. With unsaturated hydrocarbons this is apparently not difficult. A solution of the problem with the lower paraffins should yield to a systematic search for suitable catalytic material.

HYDROGENATION

The systematic investigation of the problem of hydrogenation was undertaken at the close of the nineteenth century by Sabatier and his co-workers, of whom Senderens may principally be mentioned. Isolated observations had earlier been made and recorded concerning interaction of substances with hydrogen in the presence of a catalytic material. Generally, finely divided platinum was the agent employed. Its activity in promoting oxidation as manifested in the early work of Davy and Doberemer had led to its trial in many other directions, sometimes with success. Thus, the catalytic reduction to ammonia of oxides of nitrogen by means of hydrogen in the presence of platinum sponge was recorded by Kuhlmann in 1838.[5] Carenwinder[6] showed its catalytic effect in promoting the combination of hydrogen and iodine. Applied to organic reactions, it was observed by Debus[7] that platinum black assisted the reduction of hydrocyanic acid to methylamine, and that ethyl nitrite could be transformed by means of hydrogen into ethyl alcohol and ammonia. The catalytic addition of hydrogen to unsaturated hydrocarbons and their transformation to saturated hydrocarbons was demonstrated by De Wilde in 1871,[1] platinum black being employed as agent.

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[1] D.R.P. 229406, 1909.

[2] Neumann and Jacob, *Zeitsch. Elektrochem.*, 1924, **30**, 557.

[3] B.P. 2054, 1914.

[4] U.S.P. 1092903, 1914.

[5] *Compt. rend.*, 1838, **17**, 1107.

[6] *Ann. Chim. Phys.*, 1852 (iii), **34**, 77.

[7] *Annalen*, 1863, **128**, 200.

By the researches of Sabatier and his assistants the catalytic method of hydrogenation has been generalised. From 1897 onwards, in a succession of reseaches published in the *Comptes rendus* of the Paris Academy of Sciences, by systematic application of the principle to the most diverse organic materials and employing various metals as catalytic agents, the wide applicability of hydrogenation has been made clear. The reactions have been studied generally in the vapour phase, volatile organic liquids being for the most part the materials employed in the investigation. Finely divided metals have formed the catalytic agents, and, of these, nickel, obtained freshly from the oxide by reduction, has proved to be the most efficient. The other elements which have found application are cobalt, iron, copper, platinum, and the platinum metals generally.

The simplicity of the studies carried out by Sabatier and his collaborators is striking. The procedure consisted essentially in passing hydrogen, admixed with vapours of the material to be investigated, through a tube containing the finely divided catalytic agent maintained at a controllable temperature, the products of reaction being suitably collected on emergence from the heated tube.

It was found to be essential that the hydrogen employed should be completely free from all impurities. Traces of sulphuretted hydrogen, of phosphine, arsine, and hydrogen chloride were found to act as catalyst poisons. Hydrogen, obtained by electrolysis and subsequently freed from traces of oxygen and moisture, was therefore largely employed, since by this process the other impurities could readily be avoided.

The preparation of hydrogenation catalysts. Apart from the purity of the materials employed in hydrogenation processes, the most important factor in the conduct of such reactions is the preparation of the catalytic agent in a form suitable for use and of sufficient activity for the purposes required. Certain details relative to the preparation and properties of such agents are therefore apposite.

Nickel. Catalytic nickel is the most important member of the group of hydrogenation catalysts. It is normally prepared by reduction of nickel oxide by hydrogen, an operation which can frequently be carried out in the reaction system. The oxide employed should be free, as far as possible, from the halogens and sulphur-containing compounds, since all these are catalyst poisons. Hence, where expense is not involved, the nitrate or an organic salt of nickel forms a suitable starting-point for the preparation of the oxide. The sulphate and chloride are the cheapest salts of nickel. When these are used the oxide is prepared by ignition of the hydrous oxide obtained by precipitation from solutions of the salts, followed by a thorough washing. In some cases the carbonate is precipitated. The washing of such precipitates should be continued until tests indicate freedom from the anion of the nickel salt and the cation of the precipitating agent. In the preparation of nickel supported on a finely divided support material the precipitation may be carried out in presence of the support, *e.g.* kieselguhr, and the support-precipitate mixture washed together. In this way good distribution of the support may be obtained.

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[1] *Ber.*, 1874, 7, 352.

For nickel catalyst on coarser support material, such as pumice, diatomite brick, and the like, the most convenient procedure is to impregnate the support with a hot, strong solution of the nitrate. A preliminary experiment will indicate how much liquid a given sample of support material can take up to saturation, and this ratio of support to liquid should be used. A concentration of 10 per cent nickel in the final product makes a good supported catalyst, and this figure determines, therefore, the concentration of nitrate liquor employed. To ensure thorough impregnation of the support it is a useful practice to heat the support above 100° C. and immerse it while still hot in the nickel nitrate solution.

The calcination of the nitrate, organic salt, or impregnated support to yield oxide may be conducted in a casserole over a flame which will not permit too intense calcination. The actual temperature of conversion to oxide is not a matter of great moment, the subsequent reduction temperature being the decisive factor. Some data on the effect of calcination temperature on the product have been recorded by Brown and Henke.[1] They suggest limiting the temperature of ignition to 450, as sintering is appreciable above this temperature.

The presence of small amounts of promoters in nickel catalysts invariably facilitates the preparation of an active material, and use of these materials can be generally recommended both for supported and unsupported catalysts. Ceria, thoria, and alumina are strikingly good. Medsforth[2] has recorded tests of many materials as promoters. They help to produce a more porous oxide and a more active metal. Actual concentrations of promoter cannot be laid down generally, but quantities varying between 0·5 and 15 per cent of the nickel metal are efficient. They may be introduced as nitrates into the nickel solution.

The temperature of reduction of the oxide is the decisive factor in the preparation of a nickel catalyst. Quite generally it may be stated that the higher the reduction temperature, the less active will the resulting catalyst be. Supported catalysts are less sensitive to temperature than the unsupported material. For the latter a reduction temperature of 350° C. should never be exceeded, and the lower the temperature of reduction the more active the product, although the longer is the time consumed in the reduction process. A temperature of 300° C. probably represents a happy mean between the conflicting factors for the production of a catalyst of high activity. Supported materials do not reduce so readily as unsupported catalysts, and a temperature of 350° C. can be used with equanimity. Where extreme activity is not required, reduction of supported materials may be carried out as high as 450°-500° C. Promoted catalysts, both supported and unsupported, are very much less sensitive to overheating in the reduction process than are catalysts composed of nickel alone. When reducing at the higher temperature limits, it is good general policy in catalyst preparation to use a relatively slow stream of reducing gas.

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[1] *J. Physical Chem.*, 1922, **26**, 161, 272, 324, 631, 715; 1923, **27**, 52.

[2] *J. Chem. Soc.*, 1923, **123**, 1452.

Nickel catalysts may be prepared by direct reduction of the cyanide[1] and the chloride[2] with hydrogen. This latter method is remarkable in view of Sabatier's observation that the halogens act as poisons. It merits further test of this factor. Kelber showed that the same factors as regards reduction temperature and activity operated in the reduction of the cyanide as have already been laid down for oxide reduction.

It should be borne in mind that a catalyst cannot in general be raised above the temperature of reduction without loss of activity. This is especially true of unsupported catalysts. It must be remembered, in the conduct of markedly exothermic reactions, that the heat of reaction raises the temperature of the catalyst in spots considerably above the temperature recorded on the measuring instrument used, and such localised hot-spots diminish catalytic activity. The prolonged effect of even moderate temperatures is also to transform the catalyst to a more compact mass with a resulting decrease in efficiency.

Copper. A copper catalyst is readily prepared in an active condition by reduction of the oxide at low temperatures. What has been said in the preceding paragraphs relative to precautions as to poisons, methods of oxide preparation and support materials is applicable also in the case of copper. It must be particularly emphasised, however, that the production of an active material is especially dependent on the temperature of reduction of the oxide. By lowering the temperature of reduction of a given sample of copper oxide from 200° C. to 150° C., a fivefold increase in the adsorptive capacity of the resultant copper for hydrogen was achieved and a corresponding increase in catalytic activity was secured[3]—an activity far superior to those recorded by Sabatier for copper catalysts. A temperature of 150° C. represents an impracticably low temperature of reduction of ignited copper oxide, the time required for reduction being several days, but a reduction temperature of 200° C. can be employed with quite good results. Thus Pease[4] found that such a catalyst could be used to measure the rate of hydrogenation of ethylene at 0° C. The sensitivity of the product to the reduction of temperature is probably to be ascribed to the exothermicity of the reaction. Slow rates of hydrogen gas passage are therefore to be recommended. It is a good plan to initiate reduction of copper oxide at a temperature 50 degrees above the chosen reduction temperature, and, after the process has started, to lower the temperature to that chosen. Considerable economy of time is thereby secured, as reduction occurs more rapidly at copper-copper oxide interfaces.[1]

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[1] Kelber, *Ber.*, 1924, **57**, 136, 142.

[2] Kahlenberg and Ritter, *J. Physical Chem.*, 1921, **25**, 89.

[3] Taylor, *Colloid Symposium*, Madison, Wisconsin, 1923.

[4] *J. Amer. Chem. Soc.*, 1923, **45**, 1196.

Catalysts so prepared are useful only for reactions occurring below the reduction temperature. Brown and Henke[2] found that a copper catalyst prepared by ignition of the nitrate at 115° C and reduction at 314° C was efficient in the reduction of nitrobenzene about 260° C., but deteriorated rapidly. They found, however, that a catalyst prepared from the nitrate by precipitation of the oxide with sodium hydroxide was more robust and less sensitive to temperature a fact recorded earlier by Sabatier. Apparently the product is a promoted catalyst owing its ruggedness to traces of adsorbed alkali remaining in the material. Some investigations of promoted copper catalysts should be made. Rideal and Hurst have shown[3] that copper-0·2 per cent palladium catalysts are superior to copper in the preferential combustion of carbon monoxide in hydrogen-oxygen mixtures. Brown and Henke state that small amounts of iron in the copper oxide are beneficial. Brown and Henke also studied supported copper catalysts, using pumice and asbestos. For short periods in the reduction of nitrobenzene, pumice was the better, and both were better than straight copper. For long runs the copper asbestos was superior.

Iron and cobalt. Complete reduction of the oxides of these metals can only be readily accomplished at much higher temperatures than are employed in the case of nickel and copper oxides. Consequently the catalysts show much greater tendency to sinter. It is therefore to be recommended that these catalysts be used on a support material or admixed with a promoter. Alkalis, ceria, thoria, and alumina have been used for promoted iron catalysts with good success.

Calcination of cobalt nitrate can be conducted at 400°-450° C. Reduction of the oxide at 400° C. for four hours gives an active catalyst which still contains large quantities of oxide. Reduction at 600°-700° is necessary for complete reduction of the oxide. A supported cobalt oxide can be reduced with safety in the temperature region of 450°-500° C. The reduction of iron oxide at 400°-450° C is slow, but an active catalyst is obtained even when considerable amounts of oxide still remain in the contact mass.

Platinum.—Unsupported platinum catalysts may be obtained in the form of platinum sponge, platinum black, prepared by two different methods, and as colloidal platinum. Platinum sponge is prepared by gentle ignition of ammonium chloroplatinate and is the least active of the three forms

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[1] Pease and Taylor, *J. Amer. Chem. Soc.*, 1921, **43**, 2179.

[2] *Loc cit.*

[3] *J. Chem. Soc.*, 1923, **123**, 696.

A variety of methods of preparation of platinum black have been suggested. One method is essentially that of Loew[1] and of Mond, Ramsay, and Shields,[2] which consists in the reduction of a dilute solution of chloroplatinic acid by a solution of sodium formate, followed by a thorough washing of the precipitated platinum A modification of this method employed by Willstatter and Waldschmidt Leitz[3] has been tested thoroughly and found to give excellent results.

Adams and Voorhees[4] claim that a much more active platinum black than that prepared by Loew's method is obtained by fusing chloroplatinic acid with an excess of sodium nitrate When the cooled melt is washed with water, a brown oxide is obtained which turns black during the actual hydrogenation Adams and Voorhees think that this is a black platinum oxide which loses much of its activity if complete reduction to platinum occurs, since the catalyst which has lost its activity may be revivified by shaking a short time with air. Adams and Carrothers[5] have found that in the hydrogenation of aldehydes the activity of catalysts so prepared is greatly increased by the presence of ferrous salts in the reaction system An optimum concentration of 0·0001 mol of ferrous salt per 100 c c of aldehyde reaction mixture was obtained

Colloidal sol catalysts.– Colloidal sols of the metals platinum and palladium, dispersed in various solvents such as water, alcohols, acetic acid, or hydrocarbons, are now generally employed for the saturation of unsaturated organic substances in the organic chemical laboratories The simple sols prepared by electric dispersion methods or from the double chlorides by reduction to metal, with hydrazine, hydroxylamine, or formaldehyde, are too sensitive to coagulation and precipitation by electrolytes to render them of any great utility, and, in consequence, protected sols are generally employed Paal[6] first employed as protective agents two degradation products of egg-albumin, protalbinic and lysalbinic acid[7] Albumin is gently hydrolysed with caustic soda and the protalbinic acid precipitated by the addition of sulphuric acid to the point of neutrality The filtrate is evaporated to a small bulk, acidified, and the lysalbinic acid precipitated is purified by dialysis In order to prepare an active platinum or palladium catalyst a dilute solution of a salt of these metals is added to a solution of the sodium salt of the protalbinic or lysalbinic acid, the metal salt being precipitated from solution The platinum protalbinate is dissolved in the smallest possible amount of caustic soda, the solution diluted with water and purified, as far as possible, from excess alkali by dialysis. On warming the solution with a few drops of hydrazine or formaldehyde a stable sol is readily obtained.

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[1] *Ber*, 1900, **23**, 289 [2] *Phil Trans*, 1895, **186A**, 637 [3] *Ber*, 1921, **54**, 113

[4] *J Amer. Chem Soc*, 1922, **44**, 1397

[5] *J Amer Chem Soc.*, 1923, **45**, 1071. See also *ibid*, 1924, **46**, 1675; 1925, **47**, 1047

[6] *Ber*, 1904, **37**, 124, 1905, **38**, 1398, 1908, **41**, 2273; 1909, **42**, 2239

[7] *Ibid*, 1902, **35**, 2105

Skita[1] suggested the protective colloid, gum arabic, as a substitute for the protalbinic and lysalbinic acids of Paal. Since the gold numbers or protective powers of these protective colloids are practically identical,[2] platinum and palladium protected by gum arabic are generally employed, being more readily prepared than Paal's products. Other protective colloids which may be employed are gelatine and occasionally dextrine or starch. The two factors to be considered in the preparation of such protected catalytic sols are stability and efficiency. The stability will be dependent on the degree of protection afforded by the colloid, most readily determined by the gold numbers. For example, for the above-mentioned protective colloids the gold numbers with gelatine as standard are

Colloid.	Gold Numbers.
Gelatine . . .	100
Albumin . . .	20
Dextrine . . .	0·66
Starch	0·40

The efficiency of the catalyst will evidently depend upon the dispersion and the extent of active surface. The addition of a protective colloid to a disperse platinum sol results in the diminution of the active surface and an increase in the stability. The inhibitive influence of protective colloids on catalytic processes was first demonstrated by Groh[3] and examined in more detail by Rideal[4] and Iredale.[5] Iredale confirmed the data of Groh that protective colloids cut down the catalytic activity of the sol, the inhibitive numbers of the various colloids being approximately the same as the gold numbers, whilst Rideal showed that there existed an optimum concentration when gum arabic was employed as protective colloid, the colloid being added before reduction of the metal salt, being 2 milligrms. of gum for every 10 milligrms. of platinum or 5 milligrms. of palladium. Rocosolano[6] obtained data on protecting a platinum sol prepared by Bredig's method with various protection agents, which confirm Iredale's observations.

If but a small amount of protection agent be employed, not all of the amicrons of the metal sol will be protected, and, on the addition of an electrolyte, these unprotected particles will coagulate with a resulting decrease in catalytic activity. Increase in the protective colloid concentration will effect a peptisation or redispersion of these. Evidently the optimum concentration of colloid is such that the sol is prepared in as disperse form as possible, but protected to the smallest extent compatible with stability in presence of the reactants. It may be noted that a concentration of one part of gelatine in a million of water may just be detected by this method of catalytic inhibition If Bredig's electric arc platinum be employed, the sol is relatively coarser than that prepared by the reduction of a soluble platinum salt in solution, and consequently the dispersive or peptising influence of the protective colloid is not so marked

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[1] *Ber.*, 1911, **44**, 2862; 1912, **45**, 1627.

[2] Gortner, *J. Amer. Chem. Soc.*, 1920, **42**, 595.

[3] *Zeitsch. physikal. Chem.*, 1914, **88**, 419.

[4] *J. Amer. Chem. Soc.*, 1920, **42**, 749.

[5] *J. Chem. Soc.*, 1921, **49**, 109.

[6] *Compt. rend.*, 1921, **173**, 41, 234.

A protected colloidal sol formed by the dispersion of an intimate mixture of the metals from a solution of the mixed salts is more effective both in respect to stability and efficiency than an equivalent sol of either of the pure metals This is indicated by the following approximate times for half completion of the hydrogenation of equal weights of sodium phenyl propiolate in solution [1]

Composition of Catalyst		Time of Half Completion Minutes
Milligrms Pd	Milligrms Pt	
10	0	7 0
5	5	5 0
1	9	11 0
0 2	9 8	7 0
0 1	9 9	12 0
0 01	9 99	30 0
0	10	39 0

Hydrogenation in the presence of metallic catalysts may conveniently be classified, according to Sabatier,[2] in three groups

(1) Reductions with simultaneous fixation of hydrogen
(2) Fixation of hydrogen by unsaturated compounds
(3) Hydrogenation with accompanying rupture of the molecule

A résumé of the typical examples of these three groups, as cited by Sabatier, is given in the following, together with a fuller description of those reactions having a more technical significance

REDUCTIONS WITH SIMULTANEOUS FIXATION OF HYDROGEN

Oxides of nitrogen. Nitric oxide is readily reduced in presence of nickel at 180° with formation of ammonia and water, the equation being

$$2NO + 5H_2 \longrightarrow 2NH_3 + 2H_2O$$

The ammonia formed has a tendency to combine with unchanged nitric oxide to form nitrogen and water · [3]

$$4NH_3 + 6NO \longrightarrow 5N_2 + 6H_2O$$

This reaction is of importance in the process, elsewhere discussed

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[1] Rideal, *Trans Farad Soc*, 1923, **19**, 1
[2] *La Catalyse en chimie organique*, 1913
[3] Sabatier and Senderens, *Compt. rend*, 1902, **135** 278.

(p. 169), of ammonia oxidation, as its occurrence in that process may diminish considerably the efficiency of such catalytic oxidation.

Nitrogen peroxide is reduced by hydrogen in presence of nickel at 180°. The ammonia formed interacts with unreduced oxides, and ammonium nitrite and nitrate are produced. Further hydrogenation yields ammonia and water:

$$2NO_2 + 7H_2 \rightarrow 2NH_3 + 4H_2O.$$

With high concentrations of nitrogen peroxide the reaction is very energetic, producing incandescence in the neighbourhood of the contact mass and frequently giving rise to explosions.

Similarly with the vapours of nitric acid, at 200° ammonium nitrate is produced, whilst at 350° nitrogen, ammonia, and water are the reaction products.

Organic nitro-compounds.—The aliphatic nitro-compounds are readily hydrogenated with nickel to the corresponding amine,

$$RNO_2 + 3H_2 \rightarrow RNH_2 + 2H_2O,$$

but at more elevated temperatures the hydrogenation may proceed still further. Thus, nitromethane yields methylamine, but may partially yield methane and ammonia:[1]

$$CH_3NO_2 + 4H_2 \rightarrow CH_4 + NH_3 + 2H_2O.$$

Similarly, aromatic nitro-compounds yield the corresponding amines. Further hydrogenation at higher temperatures yields the aromatic hydrocarbons and ammonia, whilst more elevated temperatures of reaction may carry the hydrogenation of the aromatic hydrocarbon yet further, yielding methane. Thus, in successive stages, nitrobenzene will yield aniline and water, then benzene, ammonia, and water, and with complete hydrogenation methane, ammonia, and water. By controlling the temperature the two latter reactions may be practically suppressed, and good conversion of nitrobenzene to aniline obtained.[2]

Aniline.—The vapour-phase reduction of nitrobenzene in presence of contact agents has been exhaustively studied by Brown and Henke.[3] They find that with nickel, and with cobalt containing small amounts of nickel, the reduction proceeds beyond the aniline stage, benzene and ammonia, and even methane and ammonia, being produced. With carefully controlled conditions, however, 95 per cent yields of aniline could be obtained. No azoxybenzene or azobenzene is produced. With copper and silver there is no reaction beyond the aniline stage, nor is azoxybenzene nor azobenzene produced. Copper shows a great tendency to sinter, however, with use; it should be prepared with an added promoter if its life is to be prolonged. Lead and bismuth seem to be the best catalysts if it is desired to stop the reduction at the azoxybenzene or azobenzene stages The yields of these partially reduced products progressively decrease as the catalyst is used. This appears to be due to oxidation of the catalyst metal, and the activity may be restored in part by reduction in hydrogen Thallium gave a 90 per cent yield of azobenzene at 260°, but the activity diminishes rapidly, probably owing to the metal melting Antimony, manganese, and chromium were found to have some catalytic activity, and the same was true of the lower oxides of molybdenum, vanadium, uranium, cerium, and tungsten, the first two being the most efficient in this group Alumina showed a little activity, but commercial tellurium and the oxides of calcium, barium, and silicon showed none

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[1] *Compt. rend.*, 1902, **135**, 226.

[2] Senderens, F.P. 312615/1901.

[3] *J. Physical Chem.*, 1922, **26**, 161, 272, 324, 631, 715; 1923, **27**, 52.

More recently[1] the same authors have shown that tin is an excellent catalyst for the reduction of nitrobenzene to aniline It is superior to copper at most rates of gas passage It is superior to nickel at all but the highest rates tried The catalyst is best prepared from the hydroxide by precipitation with sodium carbonate from a stannous chloride solution Oxidation of the hydroxide prior to reduction increased the efficiency of the resulting catalyst, the lower the temperature of oxidation the better the resulting catalyst The lower the temperature of reduction of the oxide the better was the resulting catalyst This catalyst is here mentioned in some detail because it is a new-comer in the ranks of reduction catalysts It would be interesting to know whether it is a hydrogenation catalyst or whether its action depends on alternate oxidation and reduction of the catalyst

On the technical side there is some evidence that vapour-phase hydrogenation has received serious consideration The patents to Legge and Adam[2] indicate that a copper catalyst is very efficient, conducts heat well, and can be regenerated Copper oxide is fused, cooled, and broken to size. Hydrogen or water gas in excess is mixed with the nitrobenzene Quantitative yields are obtained at 230° C The Badische Anilin- und Soda-Fabrik suggest[3] also a mixture of carbon monoxide, steam, and nitrobenzene with a copper catalyst They claim also the use of promoters such as the oxides of the alkali metals, phosphates, silicates, tungstates Brochet[4] has suggested the catalytic reduction of nitrobenzene in liquid media in presence of nickel

The huge quantities of aniline which to-day are employed in the organic chemical industry are produced by the reduction of nitrobenzene. For industrial purposes practically exclusive use is made of the method due to Bechamp,[5] which consists in reduction of the nitro body using iron and acids. Acetic acid, the original acid employed by Bechamp, is replaced by the cheaper mineral acids. In the reaction, which is frequently formulated by the equation

$$C_6H_5NO_2 + 3Fe + 6HCl = C_6H_5NH_2 + 2H_2O + 3FeCl_2,$$

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[1] *J. Physical Chem*, 1923, **27**, 736

[2] B P 166249 and 166283

[3] F P 511256.

[4] B P, 16936 and 22523/1913.

[5] *Ann. Chim.* [3], 1854, **42**, 186.

it is found that much smaller amounts of acid than correspond to tl stoichiometric relationships are required. Indeed, hydrochloric acid t the extent of 3 per cent of the theoretical requirements is found to l adequate; in certain cases ferrous chloride to an equivalent amour is substituted for this hydrochloric acid and, in presence of iron an water, a clean reduction of the nitrobenzene occurs. It is therefoı obvious that, in this case, it is not a question of simple reduction b means of hydrogen. The operation as conducted shows catalyti features. No single explanation of the mechanism of the process a yet finds general acceptance. According to Witt[1] the ferrous chlorid is converted by the reduction process to an oxychloride, which the interacts with the iron to regenerate ferrous chloride and to give simul taneously magnetic oxide of iron, Fe_3O_4:

$$6FeCl_2 + C_6H_5NO_2 + H_2O \longrightarrow 3FeOCl_4 + C_6H_5NH_2,$$
$$4FeOCl_4 + Fe \longrightarrow FeCl_2 + Fe_3O_4.$$

The sum-total of the reaction could then be expressed by the equatio

$$4C_6H_5NO_2 + 9Fe + 4H_2O \xrightarrow{FeCl_2} 4C_6H_5NH_2 + 3Fe_3O_4.$$

According to Wohl[2] the finely divided iron in conjunction with wate forms the reducing agent

$$C_6H_5NO_2 + 2Fe + 4H_2O \longrightarrow C_6H_5NH_2 + 2Fe(OH)_3.$$

Wohl assumes that the ferric hydroxide interacts with ferrous chlorid to give a double salt which, by further action of metallic iron, is con verted to ferrous chloride and magnetic oxide. It will be recalle however, in this connection that, in the Bergius process, water an iron react at 300° to yield hydrogen under high pressures when acid or salts, *e.g.* ferrous chloride, are employed as catalyst. It is possibl that, under the conditions prevailing in this reaction, due to the presenc of a hydrogen "acceptor", nitrobenzene, the reaction proceeds at th lower temperature. The real reducing agent would then be hydroge from the interaction of water and finely divided iron.

With other acids than hydrochloric acid the same circumstance hold. A small percentage of the theoretical hydrogen requirements ar sufficient for the conduct of the process. Furthermore, the method i not restricted to this particular nitro-compound. The reaction i generally applicable and is utilised in the organic dye-stuff industry i numerous cases with which it is beyond the scope of this volume to dea

Dinitro-derivatives yield the corresponding diamines. Nitropheno yield aminophenols with side reactions yielding ammonia, phenol, an water, and some aniline. Nitrous ethers yield the correspondin amines by reduction in presence of nickel, just as do the isomeri nitro-compounds. A production of the secondary and tertiary amin always occurs, the secondary amine generally being produced in the greatest amount. Gaudion[1] explains his results with these compounds by assuming isomerisation of the nitrous ethers in presence of the catalyst.

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[1] *J. Soc. Chem. Ind.*, 1887, 218.

[2] *Ber.*, 1894, 27, 1436, 1817.

Oximes on catalytic reduction yield primary and secondary amines. The amides of the fatty acids yield the corresponding primary amine and water with some formation of the secondary amine by rupture of the molecule and simultaneous production of ammonia.

Halogen derivatives.—Direct reduction of halogen aromatic compounds is possible, employing finely divided nickel as catalyst. The ease of reduction is a function of the compound. The presence in the ring of substituent groups such as methyl or hydroxy-radicals facilitates reduction. In general, the chloro-derivatives are the most easily reduced. The bromo-derivatives are less easily reduced, and the iodo-compounds least of all. This order is what would be expected in view of affinity relationships between hydrogen and the respective halogens. On an intermediate compound theory of catalysis also the same order would be forecasted, since nickel chloride is readily reduced by hydrogen at 270°, whereas the bromide is less easily reduced and the iodide practically not at all at such temperatures.

In exemplification of the catalytic reduction the following reactions will serve. At 270° monochlorobenzene is rapidly hydrogenated, benzene being formed. A certain quantity of diphenyl is, however, simultaneously produced due possibly to the direct action of the metallic catalyst on the chloro-derivative.

Poly-chloro-derivatives yield the reduced products in successive stages. Thus dichlorobenzene gives successively mono-chlorobenzene and benzene. From hexachlorobenzene a mixture of the tri-, di-, and mono-chlorobenzenes is obtained.

The chlorotoluenes are more readily reduced than the chlorobenzenes. Trichlorophenol gives a mixture of 70 per cent of phenol and some monochlorophenols. Chloroanilines readily yield the corresponding hydrochloride. Chloronitro-compounds suffering simultaneous reduction of the chlorine and nitro-groups also yield the hydrochlorides of the corresponding amine.

Oxygen-containing carbon compounds.—A number of oxygen-containing carbon compounds may be catalytically reduced with simultaneous fixation of the hydrogen. Thus, ethyl acetoacetate is converted to ethyl butyrate according to the equation

$$CH_3.CO.CH_2.COO.C_2H_5+2H_2 \longrightarrow CH_3.CH_2.CH_2.COO.C_2H_5+H_2O$$

This reaction is always accompanied by side reactions. A split of the molecule may occur ($CH_3.CO.CH_2$- and $COO.C_2H_5$), the products yielding further reduced substances, the former acetone and secondary propyl alcohol, the latter ethyl formate, which decomposes under the reaction conditions to ethyl alcohol and carbon monoxide. This latter may be transformed to methane during the reaction. Alternatively, condensation of the molecule may occur as a side reaction, catalytically assisted by the nickel. The hydrogen does not function in the change, the products of condensation being dehydracetic acid and ethyl alcohol, according to the equation

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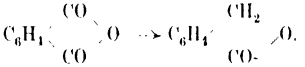
[1] *Ann. Chim. Phys.*, 1912 (viii), **25**, 129.

$$2(CH_3 . CO . CH_2 . COO . C_2H_5) = (CH_2 . CO)_4 + 2C_2H_5 . OH.$$

With nickel of medium activity aromatic ketones are reduced to the corresponding benzene derivative. Thus, acetophenone, $C_6H_5 . CO . CH_3$, yields ethyl benzene. Similarly, aromatic diketones give the corresponding hydrocarbons:

$$C_6H_5 . CO . CO . C_6H_5 + 4H_2 \longrightarrow C_6H_5 . CH_2 . CH_2 . C_6H_5 + 2H_2O.$$

The anhydrides of dibasic acids give the corresponding lactones. Thus succinic anhydride gives butyrolactone, orthophthalic anhydride the corresponding phthalide, *e.g.*



$$C_6H_4 \begin{matrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{matrix} O \longrightarrow C_6H_4 \begin{matrix} \diagup CH_2 \diagdown \\ \diagdown CO \diagup \end{matrix} O.$$

The phenols and poly-phenols may be reduced to the corresponding hydrocarbons, but the yields are low.

Aldehydes. —Aldehydes on reduction are converted to the corresponding alcohols:

$$R . CHO + H_2 = R . CH_2 . OH$$

This reaction is of prime importance in the modern work on the production of synthetic alcohol. As shown elsewhere (p. 316), from calcium carbide as starting-point, acetaldehyde may be synthesised, via acetylene, which is catalytically hydrated to yield the aldehyde. Using Sabatier's catalytic hydrogenation process, the aldehyde thus produced may be converted to ethyl alcohol. The reaction is conducted in the presence of reduced nickel at 140°, using dry aldehyde vapour and pure hydrogen. The completeness of the synthesis is limited by the reverse process of dehydrogenation of the alcohol produced, but, with careful control, a conversion of 80 per cent of the aldehyde is possible in a single passage over the catalyst. Temperature control must also be rigorous owing to the possibility of catalytic decomposition of the aldehyde, which, at 180°, under these conditions is rapidly converted to methane and carbon monoxide,

$$CH_3 . CHO = CH_4 + CO.$$

The products of reaction, consisting of alcohol, unchanged acetaldehyde, and hydrogen, are collected, and, by a process of continuous fractionation, are separated, the unchanged materials returning to the reaction system

Armstrong and Hilditch[1] *have shown that the reduction occurs more slowly than the hydrogenation of simple ethylenic compounds,* but the mechanism is the same[2] Water vapour inhibits the hydrogenation process markedly The Lonza Electrizitats Werke carry out the process technically by using a large excess of hydrogen, which is stripped of reaction product and returned to the inlet of the system

Oxides of carbon.—Both carbon monoxide and carbon dioxide may be reduced by hydrogen in the presence of metallic nickel In each case the products of reduction are methane and water, the reactions occurring being representable by the equations

$$CO + 3H_2 = CH_4 + H_2O,$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

With an active nickel catalyst the reaction with carbon monoxide may commence as low as 180°-200°, the velocity of reaction increasing rapidly with the temperature, so that at 250° the conversion is practically complete With carbon dioxide the reaction commences at a somewhat higher temperature, towards 230°, and is rapid above 300° It has been suggested that the dioxide may thus be used as a suitable starting-point for the preparation of pure methane It is necessary, however, to exercise care in the process, otherwise carbon monoxide will be found in the reaction product after removal of the carbon dioxide by alkali The occurrence of carbon monoxide in the hydrogenated products of carbon dioxide is of interest, and further study of this point should yield information on the precise mechanism of reduction

With carbon monoxide at temperatures above 250° a second reaction may occur, also catalytically assisted by metallic nickel, as well as by many metallic catalysts, *e g* iron Carbon monoxide is decomposed, yielding carbon and carbon dioxide according to the equation

$$2CO \rightleftarrows C + CO_2$$

The carbon is deposited on the nickel catalyst, rapidly rendering it ineffective catalytically.

The technical application of these hydrogenation processes to the production of illuminating gas has been the object of considerable investigation. A review of this work may therefore here be given

Technical production of methane.—Elworthy in 1902[3] was the first to apply the process of Sabatier and Senderens to the technical production of methane from carbon monoxide He employed water gas as the source of his methane. The gas was freed from carbon dioxide and so much hydrogen added that the theoretical mixture $(CO + 3H_2)$

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[1] *Proc. Roy. Soc.*, 1920, 97A, 259. [2] See p 137. [3] B.P. 12461/1902 and 14333/1904

for methane formation was obtained. The conversion was to be effected by passage of the gases over finely divided nickel at 250°. The process was to be exploited by an English company, but technical difficulties, mainly the short life of the catalyst coupled with the death of the patentee, affected the progress of the work adversely, and the problem therefore remained unsolved.

Sabatier himself attempted the solution of the problem.[1] At the outset he sought to reduce carbon dioxide by means of hydrogen at temperatures of 350°. Later he proposed an alternative process,[2] utilising the decomposition of carbon monoxide to carbon and carbon dioxide which occurs readily at 500° in the presence of a nickel catalyst, together with the observation that the carbon deposited in the mass readily combines with superheated steam to form carbon dioxide and methane. In this manner mixtures of methane, hydrogen, and carbon dioxide could be produced from water gas. The reaction could be conducted in the two stages or, by passage of suitable proportions of water gas and superheated steam simultaneously over the catalyst at 500°, the two reactions could be superimposed. In conjunction with A. Girard, considerable energy was expended in attempting this alternative scheme on economic lines, but presumably without success.

In a later patent[3] Sabatier returned to the direct reduction process, employing a low-temperature water gas with a high-carbon dioxide content and a correspondingly low content of carbon monoxide (12 per cent). In this way the necessary excess of hydrogen was obtained. The gas, after removal of the carbon dioxide, was passed first over heated copper to remove impurities, and then over the nickel catalyst to convert the mixture into methane and hydrogen.

An alternative method of producing the hydrogen-rich gas necessary for the production of methane was worked out by Bedford in the laboratories of Prof. Erdmann, Halle-a.-S., and the technical possibilities of the process were exploited by the Cedford Gas Process Co. in England.

The difficulties in the way of a technical solution of the problem of reduction of carbon monoxide by hydrogen in the presence of nickel may be briefly summarised as follows :

(1) Theoretically, three volumes of hydrogen are required for one of carbon monoxide. In technical practice, it is found that at least five volumes are requisite.

(2) Sulphur-containing gases poison the nickel catalyst.

(3) The decomposition of carbon monoxide to carbon dioxide and carbon may occur with decomposition of the latter on the nickel catalyst resulting in loss of catalytic activity.

The use of low-temperature water gas, as suggested by Sabatier, to overcome the first difficulty suffers from the disadvantage that considerable quantities of carbon dioxide must be removed, an operation of considerable expense. Alternatively, Elworthy's proposal to admix hydrogen is limited in its application by the relatively high cost of hydrogen The attainment of the hydrogen-rich gas can, however, be realised by removal of carbon monoxide from water gas, and this is possible by the physical method of liquefaction, making use of the difference in the boiling points of the two constituents ($H_2 - -252\ 5°$, $CO = -190°$) As mentioned elsewhere (see p 228), this process of liquefaction has been employed by Frank and Caro for the preparation of hydrogen

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[1] F.P. 354621/1905.

[2] F.P. 355900/1905.

[3] F.P. 400656/1908.

By a modification of the method of operation it was found possible so to conduct the liquefaction that at the temperature of liquid air so much carbon monoxide was removed from water gas that an uncondensed fraction containing 14 per cent of carbon monoxide was obtained The liquefied carbon monoxide was vaporised, a portion mixed with the 14 per cent fraction to bring it up in composition to 17 per cent, and the remainder burned in gas-engines to yield motive power to drive the compressors and also to work the pumps necessary to remove all traces of carbon dioxide from the original water gas This was accomplished by washing with water and with alkali under pressure, or according to the patent of Behrens and Behrens,[1] by alcohol under pressure in a circulatory system

The adoption of the liquefaction process to obtain the hydrogen-rich gas mixture simultaneously solved the second difficulty in the process For, in the cooling operation, it was found that all sulphur compounds were completely removed from the uncondensed portion and remained behind as solids in the carbon monoxide rich fraction A gas was obtained so free from sulphur impurities that after the passage of 500,000 litres over 200 grms of reduced nickel the activity of the catalyst was absolutely unimpaired From other sources it is possible to confirm this observation as to freedom from sulphur and it may be stated that as much as 3,000,000 volumes of gas per volume of catalyst may be successfully treated without recording a departure from the quantitative nature of the conversion

The further difficulty associated with the process due to carbon deposition, is practically eliminated by use of the gas with 5 volumes of hydrogen to 1 of carbon monoxide The diluent effect of the hydrogen is sufficiently great to prevent decomposition occurring in any marked degree

For the reduction process it was found that three quartz tubes,[2] 1·5 metres long and 12 cm diameter, each containing 200 grms of finely divided nickel, were adequate for the treatment of 400-500 cubic feet of gas per hour The yield of methane-rich gas thus obtained averaged 200-250 cubic feet per hour The quartz tubes were maintained at a temperature of 280°-300° Since the reaction is strongly exothermic,

$$CO + 3H_2 = CH_4 + H_2O + 48{,}900 \text{ cals},$$

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[1] D R P. 226942

[2] Thermal Syndicate, Wallsend

it may readily be shown that with a gas of 17 per cent carbon monoxide content the process will maintain itself without the supply of external heat.

In a sixty-hour test run under these conditions the following sample data were collected :

	CO_2	CO	H_2	N_2	CH_4	Cal Val. per cub. ft.
(*a*) Composition of the water gas .	3·8	38·3	52·2	5·7		288
(*b*) Water gas freed from CO_2 .	0	41·0	54·0	5·0		—
(*c*) Hydrogen-rich gas . .	0	13·9	84·3	1·8		298
(*d*) Carbon monoxide-rich gas .	0	93·2	0·5	6·3		325
(*e*) Mixture of (*c*) and (*d*) used for reaction . . .	0	16·3	80·9	2·8		298
(*f*) Samples after reduction . (1)	0	0	61·8	6·9	28·3	466
(2)	1·4	0·2	60·6	5·8	31·8	488
(3)	0·6	0	61·4	6·2	31·8	490

It was shown that if diminution in activity of the nickel due to carbon deposition occurred, this could be removed by slowing down the stream of gas for a period of time during which the nickel recovered its activity. According to Mayer and Henseling,[1] this is due to interaction of the deposited carbon with hydrogen to form methane.

To avoid carbon deposition, the carbon monoxide content is kept below 17 per cent Hence a gas with more than 32 per cent of methane cannot be obtained in one operation. Actually, however, by addition of further quantities of carbon monoxide to the reduced gas, the process may be repeated and a gas containing as much as 76 per cent of methane may be obtained by successive treatments.

As to the economics of the process, Mayer and Henseling are pessimistic. Erdmann, on the other hand, claims considerable possibilities for the process It is obvious that a considerable reduction in volume occurs in the process, so that large volumes of gas must necessarily be treated to obtain a given output This would militate against its successful utilisation as a source of illuminating gas *per se.* On the other hand, the considerable increase in calorific value per unit volume accompanying the conversion suggest its application as an enriching agent for water gas produced in gas-works for addition to the ordinary coal gas supply. This would obviate the use of oil supplies for carburetting water gas and therefore increase the quantities of such material available for other purposes. There seems to be distinct possibilities of use for a gas with a calorific value averaging 350 B.T.U. capable of production at a figure comparable with that of coal gas. The product of the Cedford process, it was seen, averages 480 B.T.U. per cubic foot, so that admixture of this with an ordinary water gas of 300 B.T.U. in equal proportions would yield a gas of calorific value well above the 350 B.T.U. standard. The cost of production, also, should be within the limits of practical consideration Nevertheless, so far as is known, no considerable technical development has taken place in such direction Extended familiarity with technical catalytic processes may, however, promote such development along the lines suggested by the above outline or in similar directions, employing other catalytic agents for the production of the methane

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[1] *J. f. Gasbeleucht.*, 1909, **52**, 169, 197.

Medsforth[1] has shown that this reaction can be much more rapidly conducted if the nickel catalyst contains a promoter. Ceria, thoria, glucina, chromium oxide, alumina, and silica gave a from 17-fold to 12-fold increase in velocity over that obtainable with the straight nickel catalyst. Zirconia, molybdenum, and vanadium oxides were somewhat less efficient, though still good promoters Tin and magnesium oxides, copper and silver metals produced no acceleration over the straight nickel With the carbon dioxide reaction the increases in velocity were somewhat less than those recorded for the monoxide reaction, although the order of efficiency was the same The mechanism of the promoter action has already been discussed[2]

Armstrong and Hilditch[3] conclude that when purified water gas is passed over nickel at 200°-300° C the predominating reaction is

$$2CO + 2H_2 = CO_2 + CH_4$$

The reaction is regarded as the sum of two reactions

$$2CO + 2H_2O = 2CO_2 + 2H_2,$$
$$CO_2 + 2H_2 + 2H_2 = CH_4 + 2H_2O,$$

the former of which is regarded as occurring in the same manner as the reaction in presence of copper previously studied by them,[4] namely, via formic acid.

$$CO + H_2O \longrightarrow HCOOH \longrightarrow CO_2 + H_2$$

With cobalt the reaction commences at a lower temperature, 180° C, but the reaction yielding carbon dioxide and methane is subsidiary to the main methanation process:

$$CO + 3H_2 = CH_4 + H_2O$$

Silver is inert, iron almost so, platinum and palladium of minor activity. Increase of pressure up to 6 atmospheres increased the minimum temperature of interaction The reaction producing carbon dioxide and methane produces more methane from water gas than any other reactions It may therefore have value as a means of increasing the methane content or lowering the carbon monoxide content of town's gas

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[1] *J Chem Soc*, 1923, **123**, 1452.

[2] Chapter V. p 104

[3] *Proc Roy. Soc*, 1923, **103A**, 25

[4] *Proc. Roy Soc*, 1920, **97A**, 265.

Various efforts to produce methane from carbon monoxide and hydrogen in the presence of metallic copper have thus far proved unsuccessful. This raises an interesting problem as to the reasons why nickel and copper are thus differentiated.

Partial reduction of carbon monoxide.—The possibilities inherent in a process for the conversion of water gas into methyl alcohol according to the reaction

$$CO + 2H_2 \longrightarrow CH_3OH$$

first attracted the attention of Sabatier and Senderens.[1] They found, however, that with nickel as a catalyst no trace of alcohol was obtained, the reaction proceeding entirely to methane:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O.$$

At a later date[2] the Badische Co. claimed the utilisation of pressure in a process for the conversion of blue water gas into a mixture of oils. Pressures over 100 atmospheres and a temperature range of 360°-420° C. were claimed as suitable with catalysts consisting chiefly of metals, especially iron and others of the iron group, impregnated with alkalis; in addition zinc and zinc oxide were suggested as catalysts. The oils so produced consisted in part of hydrocarbons; the rest was water-soluble containing alcohols, acids, aldehydes, and ketones.

A paper patent in 1916[3] describes the preparation of methyl alcohol from water gas at atmospheric pressures, utilising nickel or platinum as catalyst. In 1921 Calvert[4] claimed an 80 per cent conversion into methyl alcohol at atmospheric pressure. No details of the catalyst are given, but it was in all probability a metallic oxide. Patart[5] in the same year claimed the conversion of a gas mixture of composition corresponding to $2H_2 : CO$ at 300°-600° C. and at high pressures into methyl alcohol, utilising metals or oxides which are hydrogenating catalysts.

In 1923 the Badische patents appeared, and the technical plant at Merseburg was put into operation for the manufacture of pure methyl alcohol, whilst experiments on the production of long chain compounds, including alcohols and acids and hydrocarbons suitable for motor fuels, were continued by Fischer.[6] This phase of the process is at present just emerging from the experimental to the industrial stage.

It is clear that two stages in the process of reduction are distinct from one another, the primary or ready production of methyl alcohol, which is apparently followed by further reactions building up the hydrocarbon chain.

Methyl alcohol production.—From the heats of formation of the various reactants the heat of reaction to form methyl alcohol from the ideal water gas $2H_2 : CO$ is found to be 27,000 cals, the reaction being exothermic.

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[1] *Ann. Chim. Phys.* (iv.), 1905, 418.

[2] D.R.P. 293787/1913 and B.F. 468427/1914.

[3] Dreyfus, B.F. 492154/1916.

[4] *Chem. Age*, 1921, 5, 153.

[5] B.F. 540343/1921.

[6] *Brennstoff Chemie*, September 15, 1923; July 1, 15, 1924.

$$CO + 2H_2 = CH_3OH + 27{,}000$$

The values of the equilibrium constant at various temperatures may be obtained with the aid of the approximation equation of the Nernst heat theorem:

$$\log_{10} K = -\frac{Q}{4{\cdot}571\,T} + 1{\cdot}5\Sigma\nu \log T + \Sigma\nu C,$$

where C represents the chemical constants

Inserting the values $Q = 27{,}000$, $C_{H_2} = 1{\cdot}60$, $C_{CO} = 3{\cdot}5$, $C_{CH_3OH} = 3{\cdot}5$, $\nu = 2$ we obtain the following values of K_p

Temperature °K	400	500	600	700	800	1000
$\text{Log}_{10} K_p = \left(K_p = \frac{(H_2)^2(CO)}{CH_3OH}\right)$	$-2{\cdot}40$	1·88	2·94	4·72	5·98	7·80

It is clear that it is most advantageous, as in the ammonia synthesis, to operate at as low a temperature as is possible compatible with catalytic efficiency

The importance of operating at high pressures is likewise evident from the fact that the equilibrium is displaced towards the methyl alcohol side with increase in pressure proportionally to a much greater extent than in the ammonia synthesis

Thus, at 600° K or 327° C the equilibrium constant is *ca* 10^3, if water gas containing equal quantities of hydrogen and carbon monoxide be brought to equilibrium with methyl alcohol at various pressures, the partial pressures of each constituent will be

Total Pressure in Atmospheres	Partial Pressure, H_2	Partial Pressure, CO	Partial Pressure, CH_3OH
1	0·5	0·5	$9{\cdot}5 \times 10^{-2}$ mm
10·1	5	5	0·125 atm
225	50	50	125 atm

The choice of catalyst for the reaction was evidently limited by the fact that hydrogenation to methane had to be avoided More hope was to be found in substances such as metallic hydroxides, which readily yielded formates on interaction with carbon monoxide The study of the nature of the products of decomposition of metallic formates had been carried out by Gieben, Hofmann, and Goldschmidt, and whilst potassium formate yielded the oxalate and hydrogen on heating, zinc formate was found to give good yields of formaldehyde, methyl formate, and methyl alcohol.

The experiments of Patart, of the Service des Poudres Français, and of the Badische Co showed conclusively that zinc oxide was in fact an excellent catalyst, being quite active at temperatures of 400°-420° C., pressures of from 150-250 atmospheres being employed.

The Badische Co. are said to be operating at temperatures as low as 250°-300° C., with a zinc oxide catalyst promoted with chromium oxide and at a pressure of 200 atmospheres.

In operating the process, as has been indicated, special attention has to be paid in purification of the ideal water-gas mixture $2H_2 : CO$, not only in respect to sulphur compounds, but in the elimination of all traces of hydrogenating catalysts such as iron and cobalt and especially nickel salts. The catalysts prepared from oxides of metals in different systems in the periodic table, with the most basic oxide in excess, must likewise be free from these impurities as well as from alkalis. Copper has proved the most suitable metal as catalyst container.

Synthesis of hydrocarbon chains.—Whilst the primary formation of methyl alcohol on the surface of the zinc oxide catalyst apparently proceeds smoothly through the formate, the subsequent production of long chain hydrocarbons and their oxy-derivatives appears to be more complicated. As efficient catalysts, oxides or iron impregnated with strong alkalis at 400°-420° C. and 150 atmospheres may be used. The resulting product contains relatively large quantities of isobutyl and higher alcohols up to C_9, isobutyric and higher acids up to C_9, isobutyric aldehyde and higher aldehydes, acetone and higher simple and mixed ketones, about 2 per cent of esters, 1 per cent of hydrocarbons, and a small quantity of waxy solid.

The mechanism of formation of these long chains can be interpreted in various ways. Since the combination of a hydrogenating catalyst and a strong alkali are required to effect catalysis, this suggests the following sequence of reactions :

(1) $CH_3OH + CO \rightarrow CH_3COOH$ on the alkali,
(2) $CH_3COOH + H_2 \rightarrow CH_3CHO$ on the hydrogenator,
(3) $CH_3CHO + H_2 \rightarrow C_2H_5OH$ on the iron.

The process commences again with ethyl alcohol as reactant.

If this mixture be heated to 400° C. in an autoclave the alcohols and aldehydes are decomposed and a mixture of saturated and unsaturated hydrocarbons are obtained, a suggestive method for the formation of natural naphthenic petroleum from water gas.

HYDROGENATION OF UNSATURATED COMPOUNDS

By far the greater number of catalytic hydrogenation processes may be classified in this grouping, and in the hardening of oils the utility of the process finds a practical application. Examples of hydrogenation of all types of unsaturated compounds may be given, including compounds containing the ethylene double bond, the acetylene triple bond, the triple and quadruple linkage between carbon and nitrogen, the double bond between carbon and oxygen, the benzene nucleus, and various other unsaturated nuclei

Ethylene.—The ethylene linkage is readily hydrogenated in the presence of metal catalysts Thus, in the presence of nickel, ethylene itself is hydrogenated at temperatures as low as 30°, ethane being the product. The rate of reaction increases with temperature, and is very rapid in the temperature interval 130°-150°. If the temperature employed be too high, decomposition of the hydrocarbon, in other words, dehydrogenation, also sets in, with deposition of carbon and liberation of a mixture of ethane, methane, and hydrogen, the two latter in larger quantities the higher the temperature employed. This behaviour is quite general for all the ethylene hydrocarbons investigated At the lower temperatures hydrogenation proceeds more or less quantitatively to the corresponding saturated compounds. At elevated temperatures decomposition sets in, with formation of simpler hydrocarbons and hydrogen together with carbon and a small proportion of complex liquid hydrocarbons.

Mechanism—The best kinetic studies of the hydrogenation of ethylene have been made by Rideal[1] using a nickel catalyst and by Pease[2] with copper Rideal used a relatively inert nickel catalyst produced on a strip of nickel foil. He studied the rate of reaction of the mixed gases, at relatively low partial pressures (0-200 millimetres), in varying ratios, over the temperature interval of 30°-200° C He found that, in excess of hydrogen, the velocity is proportional to the pressure of ethylene, in excess of ethylene to the hydrogen partial pressure Ethane acts as an inert diluent. An optimum temperature of reaction occurs at about 137° C The reaction velocity is governed not only by the rate of impact of the reactants on the free spaces of the catalyst, but also by the length of life of the molecules on the surface These contrary factors gave a maximum velocity effect at 137° C Rideal made the important observation that, on the most advantageous conditions of impact, the catalytic efficiency of his metal surface was only 0·04 per cent Oxygen inhibits the reaction, hydrogenation of the ethylene being negligible before all the oxygen is converted to water. From his data, Rideal deduced a heat of adsorption of hydrogen by nickel of 12,000 cals, a surprisingly high value which was, however, subsequently confirmed by direct measurement[3]

Pease showed that, in presence of copper, the bulk of the surface in contact with a stoichiometric mixture is largely covered by ethylene, and the rate of reaction is determined by the rate at which the hydrogen can reach active centres in the catalyst surface. Pease showed that the centres on the copper surface which are capable of adsorbing hydrogen were not all sufficiently active to produce hydrogenation, and that therefore, even in a very highly active catalyst (Pease's catalysts were so active that the reaction was rapid at 0° C.), the proportion of the surface which was catalytically efficient was a very small fraction of the total surface. This confirmation of Rideal's result in the case of nickel is of fundamental importance in the theory of contact catalytic change.[1]

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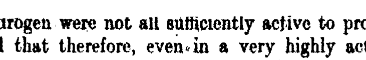
[1] *J. Chem. Soc*, 1922, **121**, 309; see also Palmer, *Proc. Roy Soc*, 1921, **99A**, 402.

[2] *J. Amer Chem. Soc.*, 1923, **45**, 1196, 2235; see also Grassi, *Il Nuovo Cim*, 1916 (6), **11**, 147.

[3] Foresti, *Gazzetta*, 1923, **53**, 487, Beebe and Taylor, *J. Amer. Chem. Soc.*, 1924. **46**, 43.

The problem of hydrogenation of unsaturated hydrocarbons is allied to the experimental work of Bergius on the action of high-pressure hydrogen on coal and tar oils. Experimental investigation shows that, at 400° and 100 atmospheres hydrogen pressure, hydrocarbon oils result from coal, and that these yield, on distillation, products resembling the paraffin hydrocarbons. The application of catalytic agents to such reactions would seem to offer possibilities of development in a technical direction.

Alcohols with a single unsaturated linkage are hydrogenated, with formation of the corresponding saturated alcohol. Thus, at 130°-170°, in presence of nickel, allyl alcohol yields propyl alcohol. Similarly, citronellol,



$$(CH_3)_2C=CH(CH_2)_2.\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2.CH_2.OH,$$

yields the dihydro-derivative.

With aldehydes, conversion to the saturated aldehyde is readily effected, but simultaneous reduction to the saturated alcohol occurs, though at a less rapid rate of reaction. Thus crotonaldehyde gives a 50 per cent yield of butyric aldehyde and 20 per cent of butyl alcohol when heated with hydrogen in presence of nickel at 125°.

By adjustment of the temperature of operation, ketones with ethylene linkages can be reduced to the saturated compound without simultaneous reduction of the ketonic grouping. Thus, at 160°-170°, phorone, $(CH_3)_2C=CH.CO.CH=C(CH_3)_2$, gives di-isobutyl acetone. At 225° the corresponding secondary alcohol and saturated hydrocarbon appear in the product.

Unsaturated acids are likewise hydrogenated without any action of the acid on the metal catalyst; this is of importance in the technical hydrogenation of oils, since these always contain small amounts of free acids.

The esters and glycerides of unsaturated acids are likewise hydrogenated readily in the vapour phase. For technical operation, however, the discovery that hydrogenation could be effected in the liquid phase obviated the necessity of employing the vapours of the oils, most of which are non-volatile. A considerable industry in the hydrogenation of oils has now been established, the details of which merit extended consideration.

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[1] For further discussion see Poisons, Chapter VI. p. 127.

Hydrogenation of Oils

The classic studies of Sabatier and Senderens which have just been detailed undoubtedly laid the foundation for the development of the many processes now in technical operation for the hardening of oils by hydrogenation. The problem of oil hardening, briefly stated, consists in the conversion of oils which at the ordinary temperature are liquid into fats which are hard under the same conditions Chemically expressed, the problem is the transformation, by addition of hydrogen to the molecule, of the glycerides of unsaturated acids, such as oleic acid, into the glycerides of the corresponding saturated acids, such as stearic acid The hydrogenation is accompanied by the elevation of the melting point of the glyceride Since the market value of solid or semi-solid fats is intrinsically higher than that of the liquid fats, it is obvious that such a transformation, if effected cheaply, has a large industrial importance in the soap, candle, and margarine industries

Early efforts to effect hydrogenation of oils are almost legion, and all of them were failures technically The early work of Chevreul and Berthelot is classic, many possible methods of introducing hydrogen being attempted Chlorine,[1] bromine, and iodine[2] have all been proposed. Nascent hydrogen produced from finely divided zinc and water in the presence of olein under pressure was claimed by Tissier[3] Schmidt's process of heating zinc chloride with oleic acid at 185° was tried, without success, upon a large scale The process of Warentrapp, in which olein is fused with caustic potash with formation of palmitic acid, had an industrial application so long as the price of olein was low The brisk advance in recent years of the price of this material has, however, destroyed the value of the process The processes of Wilson and of Milly transformed oleic acid into oxystearic acid by the action of sulphuric acid. The losses in the process are, however, considerable and militate against its use Hydrogen generated by electrolysis was also tried by Petersen, who electrolysed alcoholic solutions of oleic acid acidified with a mineral acid, nickel electrodes being employed The yields obtained did not exceed 20 per cent Aqueous fatty material acidified with sulphuric acid and electrolysed, as well as material previously sulphonated,[4] with subsequent electrolysis, have also been proposed as solutions of the problem De Hemptinne employed the electric discharge upon a thin layer of oil in contact with hydrogen Repeated operation thus gave yields up to 40 per cent

Hydrogenation by catalytic action was shown by Sabatier and Senderens to be easy of accomplishment with bodies capable of vaporisation. The patent of Senderens[1] for the reduction of the vapours of nitrobenzene to aniline by hydrogen in presence of finely divided nickel is the first patent significant of the technical development which such catalytic hydrogenation would rapidly attain.

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[1] Zurrer, D R P. 62407/1891, Imbert, U S.P 901905/1908

[2] Goldschmidt, *Sitzungsber K. Akad Wiss Wien*, 1875, 72, 366, de Wilde and Geychler, *Bull Soc chim*, 1889 (iii), 1, 295.

[3] F P. 263158/1897.

[4] Waser, D.R P. 247454/1911.

Application of the principle to liquid media was disclosed in the patent of Leprince and Sieveke[2] and in the corresponding British patent of Normann.[3] For this latter, which has been exploited in England by Messrs. Crosfield of Warrington, a fundamental character was claimed. It was decided (1913) in the English courts that the Normann patent could not be regarded as constituting a monopoly of processes for the hydrogenation of oils, and consequently many other patented processes are now being used for the purpose on a technical scale. The operation of the catalytic action in liquid medium has alone rendered this technical application possible, since only a small percentage of fats and oils can be vaporised without decomposition, rendering inapplicable, therefore, the well-known procedure of Sabatier and Senderens in the vapour phase.

The numerous processes proposed may broadly be classified under four distinct headings:

(1) Processes employing reduced nickel or other base metals.
(2) Processes employing the precious metals: platinum and palladium.
(3) Processes employing oxide of nickel and oxide catalysts in general.
(4) Processes employing organic salts of nickel.

Processes employing reduced nickel or other base metals.—These processes are applications to liquid media of the Sabatier-Senderens hydrogenation reaction. Nickel is known to be the best catalytic agent of the series, copper, iron, cobalt, and other metals having also been studied.

The preparation of the catalyst material is the most important matter in the attainment of efficient hydrogenation, the aim of the operation being the preparation of the metal in a finely divided condition. The researches of Sabatier and Senderens have shown, as previously emphasised, that the temperature of reduction of the oxide by hydrogen determines largely the properties of the catalyst. The oxide should be prepared from salts free from chlorine and sulphur, which act as poisons in the case of nickel. Copper is less sensitive to poisons, but also less active catalytically. The access of air or oxygen to the catalytic material should also be prevented, as oxidation readily occurs, even if the preparation be not pyrophoric.

The catalyst may be employed without any supporting material, intimacy of contact and uniformity being secured by agitating the oil.

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[1] F.P. 312615/1901.

[2] D.R.P. 141029/1902.

[3] B.P. 1515/1903.

A process by Kayser has been patented on this principle[1] The early patent of Normann indicates the possibility of rendering the catalyst more active by fixing it upon a porous support such as pumice The use of other supports has also been proposed, as, for example, wood charcoal, metals, talc, kieselguhr, and infusorial earths generally.

The reduction may be carried out on the oxide either in the dry state or, alternatively, suspended in a portion of the oil to be hydrogenated. The former is the familiar laboratory process modified to technical conditions While the catalyst produced may not be so active, it is more rugged than that reduced in oil. This latter method gives a catalyst which is very finely divided and of high activity. The colloidal nickel so produced, however, occasionally shows a tendency to agglomerate and to settle out of the oil mixture. The temperature of reduction of the oxide is sufficiently high that danger of altering the molecular condition of the oil by polymerisation—with consequent changes in taste—is possible and may adversely affect the hydrogenation product, if required for edible purposes Dewar and Liebmann[2] showed that it was possible to lower the reduction temperature of nickel oxide by admixing with the oxide 10 per cent of cupric oxide. The lower reduction temperature thus secured would favour the production of a more active nickel Armstrong and Hilditch[3] have shown that the copper-nickel oxide mixture must be achieved under certain prescribed conditions for the beneficial action on the temperature of reduction to be obtained They ascribe the lowering of the reduction temperature to the effect of local overheating produced by the exothermicity of the reduction process in the case of copper oxide Kahlenberg and Ritter[4] found that a 50 50 nickel-cobalt catalyst was superior to their nickel catalyst similarly prepared

The temperature at which hydrogenation is carried out is governed by the nature of the compound to be treated and the catalytic agent used. For each compound there is a well-defined range of temperature for efficient operation. With nickel, for a number of oils, the range is from 160° to 200° with a temperature of maximum saturation velocity in the neighbourhood of 180°. With copper, the temperature is 200° and upwards.

Hydrogenation with base metal catalysts is carried out technically both at atmospheric pressure and under pressures of several atmospheres, the actual procedure adopted varying with the process employed. In certain processes the hydrogen under pressure is utilised to assist in spraying the oil in the hydrogenation chambers In all cases the employment of pressures above the atmospheric will assist the progress of the catalytic action. The figures of Shaw[5] on the hydrogenation of oleic acid for the same period of time under varying pressures demonstrate the effect of pressure in diminishing the iodine value, and therefore also in raising the melting point of the material:

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[1] U.S.P. 1004035/1911.

[2] B.P 12981/1913 and 15668/1914.

[3] *Proc. Roy. Soc.*, 1922, 102A, 27.

[4] *J. Physical Chem.*, 1921, 25, 89.

[5] [illegible]

Pressures in Atmospheres.	Temperature.	Iodine No.
5	250°	77
25	250	64
50	250	52

Processes employing the precious metals.—The metals platinum and palladium, owing to their well-known catalytic activity, have received considerable study as agents for hydrogenation, and latterly their employment upon a technical scale, in spite of their rareness and consequent initial cost, has been successfully achieved.

The prevailing advantage in the use of rare metal catalysts would seem to lie apparently in the lower temperature of hydrogenation required. Thus, as early as 1906, Fokin had shown that, using palladium as palladium black, oleic acid could be reduced completely to stearic acid at a temperature of 80°-90°, whereas with reduced nickel a temperature 100° higher would be required in practice. With platinum in the form of platinum black the degree of reduction was not so great, only 24 per cent of stearic acid being formed.

The theoretical investigations of Paal and his co-workers,[1] of Willstätter,[2] and others have demonstrated conclusively that numerous hydrogenations can be effected in presence of finely divided platinum or of colloidal palladium as catalyst. In general it was found necessary to stabilise the colloidal metal, and various protective colloids were employed to effect this. Paal made use of a water-soluble protective colloid, the sodium salts of protalbinic or lysalbinic acids. Skita, who in his book *Über katalytische Reduktionen organischer Verbindungen*[3] has detailed in a comprehensive manner the literature of the subject, employed an acid-stable protective colloid such as gum arabic in place of the agents used by Paal. Solutions of platinum or palladium chloride in presence of such protective agents are reduced to stable colloidal solutions of the metal by means of hydrogen in the cold. The protective colloid also has the power of preventing the precipitation of the hydroxide of the metal when sodium carbonate is added to the solutions, the metal remaining in colloidal suspension. Such colloidal suspensions have proved to be excellent hydrogen carriers for hydrogenation of both aromatic and aliphatic unsaturated compounds. For technical operation, however, such stabilised colloidal catalytic agencies have little value, and the solution of the problem of technical hydrogenation by catalysts of the precious metal type was sought in another direction.

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[1] *Ber.*, 1905–1909, 38, 40, 41, 42.

[2] *Ibid.*, 1908, 41, 2199.

[3] F. Enke, Stuttgart, 1912.

Paal and the Vereinigte Chemische Werke of Charlottenburg have obtained numerous patents claiming the use of the noble metals for technical hydrogenation The salts of the metals are employed in a powdered state, mixed with the fats to be hydrogenated, and treated with hydrogen at a pressure of several atmospheres at temperatures preferably below 100°.

The salts employed may be the simple compounds, $PdCl_2$, $PtCl_2$, $PtCl_4$, or the chloroplatinates, such as H_2PtCl_6, K_2PtCl_6, or the copper salt. Other acid radicals, e.g. the oxalate, may be substituted for chloride They may be brought into the reaction medium either in the powdered state or in aqueous solution, or they may be added to the mass in a suspension in oil obtained by trituration of the solid with a small quantity of the oil to be hardened In general, to prevent the formation, during reduction, of free acid from the salts employed, a sufficient quantity of a neutralising agent, such as anhydrous sodium carbonate, is also added The use of carriers and porous supports for the metals is also indicated Precipitated oxides and carbonates, talc, and infusorial earths are suggested Further, metallic powders such as magnesium or nickel may also be employed to the same end It is important both in the employment of double salts of the platinum metals and of metallic supports that metals should be employed which do not act anti-catalytically in the process Thus in this connection it is to be observed that lead acts very markedly as anti-catalyst. The researches of Karl[1] have shown that hydrogenation is very slight when lead, aluminium, iron, or zinc are used as metal supports. Oxides, hydroxides, and carbonates of the first three metals have a similar anti-catalytic effect

The use of the metallic salts is much more effective from the hydrogenation point of view than the use of corresponding amounts of the rare metals in the form of the sponge or of the metal black, both the velocity and the degree of hydrogenation being markedly improved. The time required for reduction depends upon the amount of rare metal salt used and also upon the pressure of the hydrogen In an example cited by Paal in a patent specification, using 1 part of palladium as salt with 50,000 parts of castor oil, at a hydrogen pressure of 2-3 atmospheres and at a temperature of 80°, the completion of the reduction process, as recognised by the gas pressure remaining constant for some considerable time, could be attained in from six to eight hours

The recovery of the catalyst after use is an operation of importance when a catalyst of considerable costliness is employed. The methods employed consist in the main of the destruction of the colloidal nature of the catalyst and the consequent precipitation thereof This is attained by the addition of an electrolyte such as hydrochloric acid or of aluminium chloride, which electrolytes produce an immediate flocculation. With such means it has been found possible to hydro genate 100 kilos. of oil, employing 1-2 grms. of palladium, recovering from the reaction more than 90 per cent of the catalyst.

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[1] Inaugural Dissertation, Erlangen, 1911, *Ber*, 1913, 46, 3069

The use of other metals of the platinum series has also been investigated. The Vereinigte Chemische Werke[1] specifies iridium, rhodium, ruthenium, and osmium as catalytic material. Lehmann[2] hydrogenated small quantities of olive oil, starting with osmium tetroxide as catalytic material, which on hydrogenation produces a colloidal solution having markedly high activity. It is obvious, however, that the capital cost of such materials will in all cases hinder their employment upon the large technical scale.

Processes employing oxide of nickel and oxide catalysts in general.—Bedford and Erdmann[3] have claimed that oxides of nickel act as efficient carriers of hydrogen to oils and fats and that they possess certain advantages in practical employment over metallic nickel. The oxide catalyst is claimed to be less sensitive to sulphur and chlorine as poisons and to permit the use of hydrogen containing larger concentrations of impurities, notably carbon monoxide. They claimed that while both the sequioxide and monoxide are effective as hydrogen carriers, a nickel suboxide is the most efficient. A considerable patent literature arose[4] with reference to these oxide catalysts for hydrogenation and a considerable amount of technical development was initiated for such processes. It is possible that this arose in an effort to avoid infringement of patents covering the use of the reduced metal as catalyst.

A considerable controversy has taken place as to the nature of and activity of the supposed suboxide of nickel. Meigen and Bartels[5] claimed that the actual hydrogen carrier in the process was really metallic nickel. Bedford and Erdmann denied this, stating that the oil in which reduction was carried out hinders complete reduction. The catalyst upon removal from the hardened oil and after being freed from oil by benzol extraction is a strongly magnetic black powder, having a nickel content between that of the metal and nickelous oxide. It is said not to form nickel carbonyl when treated with carbon monoxide under conditions in which it would be readily obtained from the metal. Sabatier and Espil[6] found a slight inflection in the reduction rate of the oxide at a point which would correspond to a difficultly reducible oxide of the formula Ni_4O. Sabatier and Espil, however, proved the formation of nickel carbonyl with the product obtained at this stage of reduction. Moore[7] indicates the existence of a suboxide of nickel. Erdmann attempted the preparation of Moore's product, showed it to have the properties of the reduced material of Bedford and Erdmann, to show colloidal properties towards oil, and to be a good hydrogenation catalyst.

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[1] F.P. 425720/1911.

[2] *Seifen. Zeit.*, 1913, **40**, 418.

[3] *J. pr. Chem.*, 1913, **87**, 425.

[4] Bedford, B.P. 29612/1910; Bedford, Erdmann, and Williams, D.R.P. 62366; D.R.P. 260009/1911; F.P. Add. 18122/1913; Boberg and Techno-Chemical Laboratories, Ltd., B.P. 4702/1912.

[5] *J. pr. Chem.*, 1914, **89**, 301.

[6] *Compt. rend.*, 1914, **159**, 668.

[7] *Chem. News*, 1895, **71**, 82.

Armstrong and Hilditch[1] have made a thorough study of the reduction of nickel oxides of different types They conclude that the superior activity of a partially reduced product over a completely reduced metal is due to its being a "supported" catalyst, of the same type though not of the same degree of activity as nickel upon a support such as kieselguhr The reduction curves are related to the physical condition of the oxide rather than to the formation of any more or less definite suboxides They showed by experiment that the activity of a partially reduced product is dominated by the condition of the surface layer of reduced nickel. With non-supported catalysts, maximum activity is reached when only a portion of the nickel oxide has been reduced to metal, with a supported catalyst, however, which is not appreciably reduced in bulk by the process of reduction, the catalytic activity, instead of declining again, is maintained constant until and when the whole of the nickel oxide present has been reduced It is therefore certain that variations in the catalytic activity of these reduced products are to be ascribed to variations in the nature of and area of free nickel exposed, and do not require for their interpretation the assumption of the presence of any catalyst other than the metallic nickel.

That the oxide is quite unnecessary for the production of an active nickel catalyst has recently been established in two other different researches. Kahlenberg and Ritter[2] showed that nickel chloride reduced with hydrogen at 180°-250° C is a good catalyst for hydrogenation of oils Kelber[3] also showed that the characteristics of a nickel catalyst prepared by reduction of nickel cyanide with hydrogen were identical in every way with those prepared from an oxygenated starting material

Processes employing organic salts of nickel. -To avoid difficulties due to the presence of chlorine or sulphur in the catalyst preparations the use of salts of nickel containing none of these poisons is to be recommended. The organic salts of nickel have therefore been employed to a considerable degree for such purpose As examples, the use of the formate, acetate, and lactate, of nickel carbonyl and of various fatty acid and amido-salts of nickel, is indicated in the literature of the subject The use of salts such as formate and acetate forms the basis of a series of patent claims by Wimmer and Higgins[4] By employing the formate, for example, Higgins claims that the velocity of hydrogenation is accelerated by presence of the formic acid. This latter may be present to the extent of 1 or 2 per cent, and may even be introduced along with the hydrogen by passing the gas before entering the reaction chamber through a solution of the volatile acid.

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[1] *Proc. Roy. Soc.*, 1921, 99A, 490.

[2] *J. Physical Chem*, 1921, 25, 89.

[3] *Ber.*, 1924, 57, 136, 142.

[4] B.P. 18282/1912; F P. 441097/1911 and 454501/1913.

Alternatively, Wimmer and Higgins have proposed the preparation of catalysts by the reduction of such salts in a suitable protecting medium, such as the oil to be hydrogenated. After a period of time the oily mass becomes black in colour, the mixture thus obtained being added to the main body of oil to be hydrogenated. The temperature of hydrogenation is apparently 180°-200°. The nature of the catalyst thus obtained is doubtful. Commenting on these preparations, Erdmann states that the organic salts do not act themselves as catalysts. Bedford and Erdmann [1] claim that at 210° the salt is broken down, yielding the suboxide, which is the catalytic agent as in their process, whereas, at the higher temperature of 250°, metallic nickel is obtained. Incidentally, small amounts of nickel soaps result from the reaction. In order to suppress the concentration of free fatty acids resulting from such catalytic hydrogenation, Wimmer recommends the addition of drying agents to the catalytic material and proposes ignited sodium and magnesium sulphates for such purpose.

In order to promote intimacy of contact between catalyst and oil fat the use of nickel soaps as catalytic agents has been suggested. De Kadt [2] cites a mixture of the nickel and iron or copper soaps of fatty acids having a higher melting point than that of the hardened fat. After the catalytic operation is completed the soap is separated by agglomeration of the particles in the quiescent liquid or by filtration of the hot oil, the soap being retained on the filter. The aim in this method of operation is clearly to promote mutual solubility of contact material and substrate in order the more effectively to carry the hydrogen to the unsaturated fat. In the use of such materials, however, Bedford and Erdmann claim that the oxide and suboxide are the active agents.

Nickel carbonyl, $Ni(CO)_4$, the volatile compound discovered by Ludwig Mond and used so extensively in the preparation of pure nickel, has likewise been suggested as starting-point for the preparation of the catalyst. The claims of Shukoff [3] and of Lessing [4] may be mentioned in this connection. Nickel carbonyl is readily miscible with oil, and on heating to 200° is decomposed, depositing metallic nickel in a finely divided and active form. Lessing proposes the simultaneous introduction of the hydrogen and carbonyl in order to cause the formation of the metallic catalyst in the immediate presence of the hydrogen. He suggests that the gases employed need not be of great purity and that large amounts (up to 25 per cent) of carbon monoxide are permissible. Thus a hydrogen containing from 5 to 10 per cent of carbon monoxide may be passed over reduced nickel and thence direct to the oil maintained at a temperature of 200°-240°, the unabsorbed gases being returned to the starting-point for renewed passage over nickel and into the reaction mass. The amount of nickel required is said to be small, excellent results being yielded by 0·1 part of nickel per 100 parts of oil. Ellis has studied the use of nickel carbonyl and records similar results,[1] observing, however, that the greatest difficulty attending its use appears to be "the removal of finer portions of the nickel precipitate from the oil after hydrogenation but this may be accomplished by the observance of due precaution in filtration." The catalyst may, he further observes, be repeatedly used, and its regeneration is, relatively, a simple matter.

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[1] *Loc. cit.*

[2] D.R.P. 241823/1910.

[3] *E.g.* B.P. 18310/1912.

[4] B.P. 18998/1912.

Maxted[2] has studied quantitatively the inhibiting effect of carbon monoxide upon the hydrogenation of an unsaturated glyceride in presence of finely divided nickel as a catalyst. There is a very marked poisoning effect, especially pronounced at the lowest concentrations of carbon monoxide. Thus, 0·25 per cent carbon monoxide decreased the hourly absorption of hydrogen by a third, whereas an additional 1·75 per cent of the poison effected a further reduction of one-third in the amount of hydrogen consumed.

Mechanism of hydrogenation of unsaturated liquids. In the realm of solid-liquid interface reactions at metallic surfaces, the studies of Armstrong and Hilditch[3] on the rate of hydrogenation of unsaturated compounds at the surface of a nickel catalyst are both comprehensive and convincing. Several workers, such as Fokin,[4] Moore, Richter and van Arsdel,[5] Ueno,[6] Ubblehode and Svanoe,[7] and Thomas,[8] have observed an approximation to a unimolecular action in hydrogenation of liquid systems at a nickel surface. Employing as pure materials as could possibly be obtained, and working under mechanical conditions favouring maximum contact of the gaseous, liquid and solid components of the system, Armstrong and Hilditch found that unsaturated glycerides containing mixtures of olein and less saturated glycerides gave characteristic curves, more nearly a series of two straight lines than a combination of two unimolecular curves. The first (almost linear) segment corresponded to the portion of the process in which analysis of the product has shown that the main action is the transformation of less saturated glycerides to olein, and the second portion (not so straight) covers the part of the action in which olein (with the iso-oleins also formed in this action) is passing to stearin.

Later, Armstrong and Hilditch extended the study to suitable unsaturated organic individuals which could be obtained in a state of greater purity than the non-volatile glycerides. The linear character of the absorption of hydrogen-time curves became very definite. It was also shown how the linear curves could be transformed into unimolecular curves (i.) by the presence of a substance which slowly combines with the catalyst to form a permanent compound (permanent catalyst poisoning) or (ii.) by the accumulation of gaseous impurities in the gas-space above the acting system (thereby altering the otherwise constant concentration of hydrogen above the liquid). A further possibility resulting from this latter effect is that such gaseous impurities may have been preferentially adsorbed by the nickel catalyst and thus exercised a retarding influence on the reaction more than proportionate to their actual concentration in the gas phase. The linear curves obtained by Armstrong and Hilditch in these studies undoubtedly indicate that the chosen experimental conditions gave a catalyst surface which was, initially and for a prolonged period of time, completely saturated with reactants. The deviations from linearity in the later stages of the reaction are also to be ascribed in part to competition of reaction products for the nickel surface, since it has been shown[1] that even saturated hydrocarbon systems, *e.g.* ethane, cyclohexane, are strongly adsorbed by catalytic metals.

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[1] *Hydrogenation of Oils*, p. 97 (Constable, London).

[2] *Trans. Farad. Soc.*, 1918, **13**, 36.

[3] *Proc. Roy. Soc.*, 1919, **96A**, 137; 1920, **98A**, 27; 1921, **100A**, 240.

[4] *Zeitsch. angew. Chem.* 1908, **22**, 1451, 1492.

[5] *J. Ind. Eng. Chem.*, 1917, **9**, 451.

[6] *J. Chem. Ind. Tokio*, 1918, **21**, 749.

[7] *Zeitsch. angew. Chem.*, 1919, **32**, 257, 276.

[8] *J. Soc. Chem. Ind.*, 1920, **39**, 120.

Throughout the preceding work the operating pressure of hydrogen gas was maintained constant. In a subsequent contribution Armstrong and Hilditch[2] discussed the influence of variation in the hydrogen pressure. In this investigation the greater complexity of the bimolecular reaction at an interface reveals itself quite definitely.

(i.) *Normal.* In the absence of substituent groups of the kind discussed below, (iii.), and in presence of sufficient nickel (in general, so long as at least 0·1 per cent of nickel is present), the ethylenic union is hydrogenated at a rate which is in almost exact proportion to the absolute pressure of the hydrogen.

(ii.) *Subnormal.* At very low concentrations of catalyst (say 0·01 to 0·02 per cent of nickel reckoned on the organic compound) the increase in rate of hydrogenation becomes less than proportional to the increase in pressure. The compounds which absorb hydrogen most readily are in general more prone to show this subnormal effect when the catalyst concentration is diminished, and it is especially marked in the case of multi-ethylenic compounds such as derivatives of linoleic acid or linolenic acid or with citral.

(iii.) *Abnormal.* If the unsaturated compound contains another group which has affinity towards nickel (but is not open to hydrogenation), it is found that increase in hydrogen pressure causes an increase in the rate of hydrogen adsorption in more than simple proportion to the altered concentration of hydrogen. This has been observed with unsaturated alcohols and unsaturated carboxylic acids. Unsaturated aldehydes or ketones, on the other hand, show normal or subnormal behaviour.

The results are broadly, then, that increase in concentration of hydrogen causes a directly proportionate increase in the rate of hydrogenation providing there are no disturbing factors, and that the increase in rate of hydrogenation becomes abnormally large if other groups active towards nickel but not open to hydrogenation are present. In other words, the nature of the organic compound has a determining influence on the effect of hydrogen concentration

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[1] Pease, *J. Amer. Chem. Soc.*, 1923, **45**, 1196; Dougherty and Taylor, *J. Physical Chem.*, 1923, **27**, 533.

[2] *Proc. Roy. Soc.*, 1921, **100**A, 240.

By analogy with results of Rideal and Pease on the mechanism of hydrogenation of ethylene at gas-solid interfaces the proportionality between rate and pressure in the normal case is to be ascribed to the fact that the extent of association between nickel and organic compound is large as compared with that between nickel and hydrogen The accessibility of the hydrogen to free nickel surface (which will be small) varies directly as the hydrogen pressure In the subnormal cases it is apparent also that the low concentration of nickel means a still lower accessibility of hydrogen to free nickel surface, the reduction in catalyst quantity being less unfavourable to the more strongly associated reactant, the unsaturated body In the case of abnormal variation with pressure, the abnormality apparently lies in the secondary association of nickel with the unsaturated body at the second group which is not subject to hydrogenation If it be assumed that this is a position of stronger association with nickel than the unsaturated linkage which can be hydrogenated, it follows that the influence of increased hydrogen pressure will be greater than in the case where only one type of association between nickel and unsaturated body is possible It will need careful and painstaking research to verify such a point of view quantitatively The work of Langmuir and Hardy previously cited is a beginning in that direction Progress, however, may come more rapidly by the study of mechanism in vapour phase-reactions, where, as Pease has shown, it is possible more easily to follow the variation of interfacial concentration

HYDROGENATION OF UNSATURATED COMPOUNDS (*continued*)

The acetylene linkage.—This is extraordinarily readily hydrogenated in presence of metallic catalysts With nickel, acetylene and hydrogen in the volume ratio of 1 . 2 react so intensely that, with gas and catalyst originally cold, sufficient heat is developed to raise the temperature of the nickel to 150° The product is a mixture of unchanged acetylene, some ethylene and saturated hydrocarbons, together with some carbon as a decomposition product Excess of hydrogen favours ethane production. With excess acetylene, complex hydrocarbons, aliphatic, aromatic, and hydroaromatic, may be recovered from the product Ross Culbertson and Parsons[1] have studied in detail the hydrogenation of acetylene to give ethylene. Nickel was employed as catalyst. They showed that, initially, a hydrogen-acetylene mixture gave mainly ethane. This they ascribe to hydrogen already adsorbed by the nickel. When such hydrogen is consumed a product containing 80 per cent ethylene is obtained, the best results being given when the hydrogen is in slight excess of theory. As the acetylene in the mixture is increased, the ethane produced decreases and the sum of the ethylene and acetylene increases. The authors showed that both ethylene and acetylene will undergo hydrogenation at a temperature as low as $-10°$ C. with an active nickel catalyst. Paal and his co-workers[1] found that combination of hydrogen and acetylene occurs when a mixture of these gases is shaken with colloidal solution of platinum or palladium in water. With equal volumes of reactants the product contained 80 per cent ethylene. Copper is less suitable than nickel as a catalyst[2] owing to the formation of cuprene, a complex liquid hydrocarbon.

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[1] *J Ind. Eng. Chem.*, 1921, **13**, 775.

The carbon-nitrogen linkages. The triple linkage between carbon and nitrogen is readily hydrogenated with metallic nickel as catalyst. The nitriles yield the corresponding primary amine :

$$RC \cdot N + 2H_2 \longrightarrow R.CH_2.NH_2.$$

Secondary reactions occur, however, in presence of such a catalyst, and so a percentage of the product is composed of secondary and tertiary amines with an accompanying formation of ammonia :

$$2R.CH_2.NH_2 \rightarrow (R.CH_2)_2NH + NH_3,$$

$$R.CH_2.NH_2 + (R.CH_2)_2NH \rightleftarrows (R.CH_2)_3N + NH_3.$$

The quadruple linkage between carbon and nitrogen present in carbylamines $R.N:C$ is hydrogenated at 160°-180° in presence of nickel. Secondary amines of the type $R.NH.CH_3$ are the main product associated with small amounts of other amines.

The isocyanates, $R.N.CO$, yield at 180°-190° a secondary amine and water :

$$R.N:CO + 3H_2 = H_2O + NH\left\langle\begin{matrix}R\\ \\CH_3\end{matrix}\right. .$$

The water formed reacts with a portion of the isocyanate, forming a disubstituted urea $(R.NH)_2CO$ and carbon dioxide. The derivative of urea is in its turn hydrogenated, yielding water and a primary and secondary amine :

$$(RHN.)_2CO + 3H_2 = H_2O + NH_2R + R.NH.CH_3.$$

The carbon-oxygen double linkage.—Hydrogenation of the carbonyl group, CO, yields in general the corresponding secondary alcohol grouping, CH.OH. Aldehydes therefore yield the corresponding primary alcohols, with some tendency to hydrocarbon formation.

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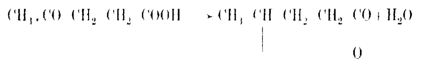
[1] *Ber.*, 1915, **48**, 275, 1195, 1202.

[2] *Compt. rend.*, 1900, **130**, 1559.

Thus at 90° from formaldehyde some methane results along with the methyl alcohol, benzaldehyde yields some benzene and toluene at 210°-235° in presence of nickel. Aliphatic ketones yield secondary alcohols with ease by catalytic reduction, and the absence of secondary reaction products is remarkable, quantitative yields being frequent. Aliphatic ketonic acids are reduced to the corresponding hydroxy-acid, subsequent elimination of water may give rise to the lactone. Thus, lævulinic acid, at 250°, with nickel, yields γ hydroxyvaleric acid, which is immediately converted to valerolactone,



$$CH_3.CO.CH_2.CH_2.COOH \rightarrow CH_3.CH.CH_2.CH_2.CO + H_2O$$

Aromatic ketones do not yield the secondary alcohol but, on the contrary, the corresponding hydrocarbon. The quinones are readily hydrogenated to the corresponding dihydroquinones.

The benzene nucleus. As is well known, the reduction of the benzene ring to more saturated cyclic products is comparatively, a difficult operation by ordinary organic processes. Thus, with hydriodic acid as reducing agent, benzene does not yield cyclohexane but the isomeric methylpentamethylene boiling at 69°. With the higher hydrocarbons, a certain quantity of open-chain aliphatic hydrocarbons always results. Moreover such a procedure is not applicable at all to many of the benzene derivatives such as phenol or aniline. Sodium amalgam and hydriodic acid have been employed with success, however, with acidic benzene derivatives.

The use of metallic catalysts has provided a method capable of fairly general application to the hydrogenation of the benzene nucleus. According to Sabatier it is undoubtedly the most important of the operations that reduced nickel has rendered possible in synthetic organic chemistry. At temperatures in the neighbourhood of 180° the aromatic nucleus may readily be hydrogenated in presence of nickel without isomerisation of the products or production of secondary reactions, and with, therefore, practically quantitative yields.

Early experiments of Lunge and Akunoff[1] had demonstrated a partial hydrogenation of benzene to cyclohexane in presence of platinum black at the ordinary temperature, or, better, at 100°. Palladium sponge, on the other hand, yielded cyclohexene C_6H_{10}. The composition of the products was deduced from the contraction in volume of the gases and is therefore uncertain. The catalytic activity of the metal also rapidly diminished. The work of Sabatier and Senderens demonstrated the efficiency of the reduced nickel catalyst.

Thus, at temperatures above 70° benzene was directly hydrogenated to cyclohexane. The velocity of reaction attained a maximum in the temperature interval 170°-190°, and in this range cyclohexane was produced practically quantitatively with a single passage over the catalyst, no side reactions occurring. At higher temperatures, more especially above 300°, some methane was produced and carbon was deposited in small amount on the nickel. The higher homologues could similarly be treated, yielding the corresponding homologues of cyclohexane. If, however, the substituent group were complex, as, for example, ethyl, propyl, butyl, etc., a certain quantity of a lower homologue of the saturated six-membered ring was simultaneously produced. Thus, for example, from ethyl benzene, in addition to ethyl cyclohexane, methane and methyl cyclohexane were produced, whilst from propyl benzene both methyl and ethyl cyclohexene resulted, in addition to the propyl cyclohexane. A high reaction temperature favours this dissociation of the molecule into simpler components, so that, in general, a temperature not higher than 180° is employed.

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[1] *Zeitsch. anorg. Chem.*, 1900, **24**, 191.

An attempt was made by Dougherty and Taylor[1] to gain some insight, by kinetic measurements, into the mechanism of the catalytic reduction of benzene to hexahydrobenzene. The results indicated that the reaction does not occur at all according to the stoichiometric equation, as calculated from gas concentrations, but at rates governed by the distribution of the reacting materials between the catalyst and the gas phase. The trend of the reaction with change of temperature was studied. It was found that, above 230° C., quantitative yields could no longer be obtained. This has also been found by Pease and Purdum[2] with copper catalysts. These can be made reactive in the synthesis, contrary to the statements of Sabatier as to the absence of catalysis with copper. The deviations from complete reaction above 230° with nickel suggests that the catalysed reaction may be the formation of dihydrobenzene, which is then further saturated in the gas phase. Water vapour in small amounts, up to 2 per cent of the hydrogen volume used in the reaction mixture, had only a slight depressing effect on the reaction velocity. Carbon monoxide in small amounts, about 2 per cent of the hydrogen volume, had a very marked poisoning effect, particularly at low temperatures of 100° or under. As the reaction temperature was raised the poisoning was less noticeable. In large quantities, however, around 50 per cent of carbon monoxide, the reaction was completely stopped at 180°. Hexahydrobenzene, at low temperature, 100° or less, had a depressing effect on the reaction velocity. This effect disappeared at higher temperatures, in the neighbourhood of 180°. From experiments at 80° and 90° C. it was shown that the temperature coefficient of the reaction measured is approximately 3·1 : 1·9 or 1·65 per 10 degree rise. This is evidently the temperature coefficient of a chemical reaction as opposed to that of a diffusion process. Pease and Purdum show that benzene depresses the reaction velocity on copper catalysts.

The reversibility of the hydrogenation processes dealt with in these

[1] *J. Physical Chem.*, 1923, **27**, 533.

[2] *J. Amer. Chem. Soc.*, 1925, **47**, 1435.

pages is most apparent in connection with the hydrogenation of the aromatic nucleus Elevation of temperature favours the reverse reaction, so that, as the temperature is raised, the yield of hydrocarbons of the cyclohexane series diminishes At temperatures above 230° the hydrogenation of the unsaturated bodies practically ceases, the reverse reaction completely predominating. Elsewhere in this book the dehydrogenation processes receive a general treatment, so that further comment is not necessary in this place beyond the statement that a study of the equilibria in such systems offers a profitable field of investigation for the physical chemist interested in the application of physico-chemical measurement to synthetic organic processes

Substituted benzenes with unsaturated linkages in the side chains are, naturally, converted by catalytic hydrogenation into the corresponding fully saturated hydrocarbons of the cyclohexane series Thus, phenyl acetylene, $C_6H_5 . C\ CH$, yields practically exclusively ethyl cyclohexane.

Hydrocarbons containing several aromatic nuclei are transformed into the corresponding fully saturated compounds Thus, diphenyl methane, $CH_2(C_6H_5)_2$, yields dicyclohexyl methane, $CH_2(C_6H_{11})_2$ Diphenyl, $C_6H_5 . C_6H_5$, yielded to Eykman[1] the compound $C_6H_5 . C_6H_{11}$, phenyl cyclohexane Sabatier and Murat[2] obtained the saturated product, $C_6H_{11} . C_6H_{11}$

Catalytic hydrogenation of the phenols, using nickel, occurs readily in the temperature interval 180°-220° The corresponding hydroxy-derivatives of the cyclohexanes are obtained Thus, phenol yields cyclohexanol with small quantities of cyclohexanone The operation is, however, more difficult with polyphenols, since the temperature limits in which the reaction can be effected are narrow If the temperature is too low, reaction velocity is small, whilst at more elevated temperatures decomposition of the molecule occurs with production of phenol and benzene, which then hydrogenate normally Derivatives of phenol such as anisol, $C_6H_5O\ CH_3$, may be hydrogenated below 150°

Aromatic alcohols are not susceptible to catalytic hydrogenation without rupture of the molecule Thus, benzyl alcohol yields toluene and methyl cyclohexane in presence of nickel at 150°

Aromatic amines, as, for example, aniline, $C_6H_5\ NH_2$ yield the cyclohexyl amine with simultaneous formation of some ammonia, benzene, and cyclohexane, in addition to the formation of some derivatives of the secondary amine, $(C_6H_{11})_2NH$ Secondary alkyl aryl amines are readily hydrogenated in the aromatic nucleus at 160°-180°, thus methyl aniline yields methyl cyclohexylamine

With aromatic acids the catalytic activity of the nickel ceases after a very brief interval, as was shown by Sabatier and Murat[3] By hydrogenation of the esters, however, with subsequent saponification these authors obtained an 80 per cent yield of the hexahydro-acid

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[1] *Chem Weekblad*, 1903, 1, 7

[2] *Compt. rend.*, 1912, 154, 1390

[3] *Ibid*, 923

Miscellaneous ring structures.—The hydrogenation of ring structures, other than the aromatic ring, follows the same general principles as are outlined above for the benzene derivatives. The stability of the saturated ring, however, determines whether the end product is ring or open chain. Thus, cyclopropane yields propane. Cyclobutene gives first cyclobutane and then by further hydrogenation yields butane. Cyclopentadiene yields cyclopentane. Cyclohexene and cyclohexadiene both yield cyclohexane.

Tetravalent terpenes fix two molecules of hydrogen. The divalent terpenes fix one molecule. Thus, limonene, menthene, and cymene all yield menthane.

Naphthalene yields tetrahydronaphthalene with nickel at 200°. At 175° the hydrogenation may proceed further to decahydronaphthalene or naphthane. Similarly, the naphthols yield the corresponding decahydronaphthols. With anthracene, likewise, the hydrogenation is the more complete the lower the temperature at which the reaction is conducted.

Considerable technical development has occurred recently in the hydrogenation of naphthalene, the products tetrahydronaphthalene, decahydronaphthalene, and a mixture of the two, marked as "Tetralin Extra", have become familiar in the last few years. A factory of the Tetralin G.m b H. at Rodleben, near Breslau, has a plant with a daily capacity of 120 tons of the tetra-derivative. The technical problem is largely one of purification, the removal of thio-bodies from the material. This is attempted by a process of adsorption from the fused naphthalene by such agents as fuller's earth and kieselguhr, together with an alkali metal or even with spent nickel catalyst. The hydrogenation process is carried out in fused naphthalene at a temperature of 180-200° C. under a working pressure of 15 atmospheres of hydrogen, a supported nickel catalyst being used. The hydrogenated products have found use as a turpentine substitute and as solvents.[1] The tetrahydro-derivative appears to be a promising material as starting-point for a new series of dyes. A very complete study of the hydrogenated naphthalenes has been given by Schroeter.[2] Braun and Kirschbaum [3] have extended Schroeter's studies to the hydrogenation of indene and acenaphthene in the pure liquids with nickel catalysts.

Heterocyclic compounds may be reduced in presence of nickel. Pyrrol gives a 25 per cent yield of pyrrolidine. Pyridine is only slowly reduced, but yields open-chain compounds and not piperidine. Quinoline gives an excellent yield of tetrahydroquinoline.

Hydrogenation with Rupture of the Molecule

As exemplified in several instances cited in the previous sections, hydrogenation in presence of metallic catalysts results in a rupture of the molecule in addition to hydrogenation of the molecule and of the products of the rupture. Thus there is a general tendency for long-chain hydrocarbons to break down into simpler molecules during the hydrogenation process. Similar behaviour was noted with the substituted benzene hydrocarbons. The production of hydrocarbons other than ethane in the hydrogenation of acetylene is to be attributed to the same cause, the setting at liberty of the two CH radicals leading to combinations of various forms. Sabatier and Senderens, by treating acetylene with hydrogen in presence of nickel, obtained as much as 20 c.c. of a clear yellow liquid quite comparable with natural petroleum, possessed even of a slight phosphorescence as is usual with the natural product, and in which higher saturated hydrocarbons, such as pentane, hexane, heptane, octane, nonane, decane, etc., were all present. By suitable modifications of the *modus operandi*, yields of liquid could be obtained with properties corresponding in different samples with the various petroleums from different oil-bearing districts. The different types of oils were produced with such success that Sabatier suggested the theory that many such natural oils had been formed in such manner by catalytic action of metals on mixtures of gases in the earth's interior. This work forms an important contribution to the subject of the origin of petroleum oils.[1]

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[1] Vollmann, *Farben-Zeit.*, 1919, **24**, 1689. [2] *Annalen*, 1922, **426**, 1. [3] *Ber.*, 1922, **45**, 1680.

The anhydrides of fatty monobasic acids rupture when hydrogenated at 180° and yield an acid and an aldehyde

$$(R.CO)_2O + H_2 \rightarrow R.COOH + R.CHO$$

The latter is, naturally, partially reduced to the corresponding alcohol in the process.

Hydrogenation of ethers is difficult catalytically, but when conducted above 250° rupture occurs, yielding the hydrocarbon and alcohol corresponding, the latter itself being further ruptured in part, *e.g.*

$$(C_2H_5)_2O + H_2 \rightarrow C_2H_6 + CH_3.CH_2.OH,$$
$$CH_3.CH_2.OH \rightarrow CH_3.CHO + H_2 \rightarrow CH_4 + CO + H_2$$

The action in the case of alkoxy-derivatives of benzene has already been cited. Below 150° they hydrogenate normally in the nucleus. A certain amount of rupture simultaneously occurs, yielding cyclohexane and the aliphatic alcohol. Above 300°, however, no hydrogenation of the nucleus occurs, and the products are phenol and the aliphatic hydrocarbon or benzene and the aliphatic alcohol

$$C_6H_5.OR + H_2 \rightarrow C_6H_5.OH + RH,$$
$$C_6H_5OR + H_2 \rightarrow C_6H_6 + ROH$$

Numerous examples of rupture of nitrogen-containing compounds have already been cited.

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[1] Sabatier and Senderens, *Compt. rend.*, 1899, **128**, 1173; 1900, **131**, 187, 267; 1902, **134**, 1185.

Selective hydrogenation.—The term selective hydrogenation may be used to indicate the preferential saturation of one or more double bonds in compounds containing several unsaturated centres. Several examples of such selectivity have already been discussed. Thus, unsaturated ketones may be catalytically converted to the saturated ketone without simultaneous reduction of the ketonic grouping. Unsaturation in a side chain may be removed without hydrogenation of the benzene nucleus. The problem acquires both theoretical and technical significance when reference is made to the selective hydrogenation of ethylenic bonds in long hydrocarbon chains. In the hydrogenation of oils the possibility exists of the conversion of the less saturated glycerides of linoleic and linolenic acids into glycerides of oleic acid before the latter are transformed into stearin.

Paal and his co-workers,[1] in their studies of catalytic hydrogenation in presence of the colloidal platinum metals, showed that such a stepwise reduction could be achieved in this manner when the two double bonds in the compound were separated by more than two carbon atoms. They showed, on the other hand, that, with a system of conjugated linkages $C:C\cdot C:C$ no selective hydrogenation occurred, the completely saturated product being produced.

H. K. Moore, Richter, and van Arsdel,[2] from a study of the rate of hydrogenation of cotton-seed oil, concluded that the process was selective, linolein passing to olein before any appreciable amount of olein was hydrogenated. Hilditch and C. W. Moore[3] showed, by analysis of samples withdrawn at intervals from the hydrogenation system, that, in a wide variety of oils (cotton-seed oil, ethyl esters of cotton-seed oil acids, maize, soya bean, and linseed oils), hydrogenated at 180° C. with nickel and, in some cases, with copper catalysts, the amount of saturated derivatives present does not sensibly increase until the amount of linoleic derivatives has fallen to 10 per cent or less of the mixture. Correspondingly, the percentage of oleic derivatives increases at the expense of the linoleic compounds up to the same point. The free fatty acids from cotton-seed oil constituted an exception in which the hydrogenation was only partially selective. Richardson, Knuth, and Milligan[4] have recently confirmed this conclusion with cotton-seed oil in presence of nickel, using a new method of analysis of the various products. They find the selectivity of the hydrogenation process to be more marked with increasing amounts of catalyst and with increasing temperatures up to an optimum in the neighbourhood of 200° C. More recently[5] the same authors have shown that with marine oils, such as menhaden or whale oil, the more highly unsaturated glycerides are hydrogenated without formation of substantial quantities of completely saturated bodies. An abrupt change occurs at an iodine value of approximately 84, at which nearly all the esters of more than two double bonds have disappeared. Below this critical point, hydrogenation results both in the formation of saturated acids and in the conversion of C_{20} and C_{22} acids containing two double bonds to corresponding acids of one double bond. Here, evidently, the principle of selectivity is only partial. One may venture as a possible explanation the view that the members non-selectively hydrogenated may have a conjugated double bond system, as indicated earlier in reference to the work of Paal.

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[1] *Ber.*, 1912, **45**, 2221.

[2] *J. Ind. Eng. Chem.*, 1917, **9**, 451.

[3] *J. Soc. Chem. Ind.*, 1923, **42**, 15T.

[4] *J. Ind. Eng. Chem.*, 1924, **16**, 519.

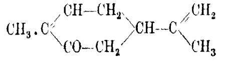
[5] *J. Ind. Eng. Chem.*, 1925, **17**, 80.

The several facts disclosed by these researches indicate that the relative extents of adsorption of the more and less saturated compounds is one of the factors which determines the selectivity of the hydrogenation process. One would conclude from the results that the more highly saturated glycerides are preferentially adsorbed to a marked degree, especially in the lower temperature interval. As the temperature rises beyond 200° C. this preferential adsorption becomes less pronounced. Furthermore, preferential adsorption should, from these results, be less marked in the case of the acids than in the case of the glycerides. While quantitative data on selective adsorption in liquid systems of this kind are almost entirely lacking, the conclusions cited are to be anticipated from adsorption studies in solid-gas systems. There is a fruitful field for investigation here, preferably with simpler unsaturated systems than are the natural oils.

Rideal[1] has studied the relative rates of hydrogenation of the sodium salts of cinnamic and phenyl propiolic acids in presence of palladium sol protected by gum arabic. He found that at low sol concentrations, the phenyl propiolate is hydrogenated at approximately twice the rate of the cinnamate under the same experimental conditions. This suggests that the salt is not desorbed from the sol surface until completely saturated and that the propiolate takes up two hydrogen molecules in the same time as the cinnamate takes up one.

Armstrong and Hilditch have recently indicated[2] the variability of the selective nature of the process with different organic molecules. Cinnamic aldehyde is first hydrogenated to phenyl propionic aldehyde. This latter is reduced, but not as rapidly as it is formed. Phenyl propyl alcohol and the corresponding ether are the main products of the secondary reduction. Cinnamic alcohol is a quite minor product of hydrogenation.

Vavon[3] has shown that, in presence of palladium black, carvone



$$CH_3.C\begin{matrix}\diagup CH-CH_2\diagdown \\ \diagdown CO-CH_2\diagup\end{matrix}CH-C\begin{matrix}\diagup\!\!\diagup CH_2 \\ \diagdown CH_3\end{matrix}$$

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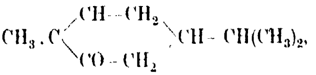
[1] *Trans. Farad. Soc.*, 1923, **19**, 90.

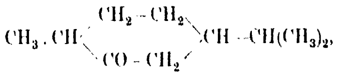
[2] *Chemie et Ind.*, August 12, 1924.

[3] *Compt. rend.*, 1911, **153**, 68.

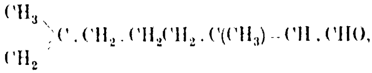
is transformed by hydrogen into carvotanacetone



then into tetrahydro-carvone

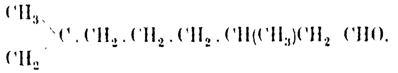


and finally into the corresponding secondary alcohol. Armstrong and Hilditch observed the same reaction with nickel. They also have shown that citral,



$$\left.\begin{matrix}CH_3\\CH_2\end{matrix}\right\rangle C.CH_2.CH_2CH_2.C(CH_3)=CH.CHO,$$

gives, first of all, citronellal,



$$\left.\begin{matrix}CH_3\\CH_2\end{matrix}\right\rangle C.CH_2.CH_2.CH_2.CH(CH_3)CH_2\ CHO.$$

Subsequent hydrogenation is characterised by a predominance of the reduction of the aldehyde group with formation of citronellol, which isomerises for the most part into isopulegol, which is then hydrogenated to menthol.

The hydrogenation of carvone differs then from that of citral in that, in the one case, the ethylenic linkage adjacent to the carbonyl group is the first to be attacked, whilst in the other case the opposite is true. In addition, the carbonyl group is the last to be attacked in carvone; in the case of citral it disappears before the second ethylenic bond is hydrogenated. Here are interesting problems in oriented adsorption, or in bond stability.

Vavon and his students have multiplied such cases of selective hydrogenation. They have studied the distribution of hydrogen between two unsaturated bodies and between unsaturated groups in the same compound.[1] The method of experimentation has in each case been the study of the rate of hydrogenation in liquid system or in solution, using colloidal platinum as catalyst. Recently, Vavon has summarised his researches [2] with a view to showing that the phenomenon of steric hindrance, familiar in esterification, addition of bromine to organic molecules, and the reactivity of oximes, is also operative in catalytic hydrogenation. Thus, in the distribution of hydrogen between an ethylenic hydrocarbon, C_7H_{14}, on the one hand and either pinene or undecylenic acid on the other, the unsaturated hydrocarbon, C_7H_{14}, is progressively less hydrogenated as we proceed from ethyl propyl ethylene, the straight chain body, to trimethyl ethyl ethylene Similar results are obtained with cinnamic acid, the α- and β-methyl, and the α-dimethyl cinnamic acids

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[1] See, for example, Vavon and Kleiner, *Compt rend.*, 1923, **176**, 401; Vavon and Husson, *Compt. rend.*, 1923, **176**, 989; Vavon and Ivanoff, *Compt. rend*, 1923, **177**, 453; Vavon, *Compt. rend.*, 1910, **150**, 1127; 1911, **152**, 1675; 1911, **153**, 68.

[2] *Rev. Gen. Sci.*, 1924, **35**, 505.

CHAPTER IX

DEHYDROGENATION

Catalytic methods of eliminating hydrogen from organic compounds have become important in two branches of industrial chemistry, viz. the preparation of aldehydes from alcohols according to the equations

$$C_nH_{2n+1}.CH_2.OH \rightleftharpoons C_nH_{2n+1}CHO + H_2,$$

$$C_6H_5.C_nH_{2n}.CH_2.OH \rightleftharpoons C_6H_5.C_nH_{2n}.CHO + H_2,$$

and the cracking of hydrocarbons into fractions of lower boiling point, *e.g.* paraffins into petrols, ligroin, benzene and other aromatic polycyclic hydrocarbons.

Processes of catalytic hydrogenation are usually reversible: indeed, this is so in all cases where the products remain in the same phase during hydrogenation or dehydrogenation.

Thus, benzene can be converted into cyclohexane by hydrogenation over reduced nickel at 70°–200°. At 270°–280° cyclohexane undergoes dehydrogenation to benzene in presence of the same catalyst.

We may thus consider the reaction

$$C_6H_6 + 3H_2 \rightleftharpoons C_6H_{12}$$

as strictly reversible.

In this and in many other cases the process of hydrogenation proceeds most rapidly at low temperatures, the equilibrium amount of the unsaturated compound being negligible at the usual temperatures of operation.

With elevation of the temperature all the components of the system are usually present in sufficiently large amounts to be capable of measurement, and it is practically certain that in the hydrogenation of benzene below 270° the equilibrium constant

$$K = \frac{[C_6H_6][H_2]^3}{[C_6H_{12}]}$$

could be arrived at from either side.

Dougherty and Taylor[1] attempted to evaluate this equilibrium constant at various temperatures with nickel catalysts but obtaine no satisfactory data. Zelinski and Pawlow [1] used platinised asbesto and palladium They showed that dehydrogenation of cyclohexan was already marked at 150° C and that the action becomes rapidly more marked as the temperature rises Platinum and palladium are superior to nickel for the purposes of an equilibrium study, since the authors note that no deposition of carbon occurs even at 408° C Zelinski showed that the dehydration was selective, in that other saturated cyclic hydrocarbons could not be dehydrogenated Thus, in a mixture of cyclohexane and cyclopentane only the former underwent the dehydrogenation process, which could therefore be used as a method of separating such bodies Zelinski has applied such processes of dehydrogenation to a study of the constituents of the naphthenes in naturally occurring petroleums, and has shown that natural naphthenes of petroleum are mainly cyclical but are not hexahydroaromatic compounds [2] Cyclohexane always yields a varying amount of methane when undergoing catalytic dehydrogenation

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[1] *J. Physical Chem.*, 1923, **27**, 533.

$$3C_6H_{12} \longrightarrow 2C_6H_6 + 6CH_4,$$

whilst methane resulting from the hydrogenation of carbon monoxide at 180°-200 in the presence of reduced nickel commences to undergo dehydrogenation with the deposition of carbon at 350-390

$$CH_4 \rightarrow C + 2H_2$$

Owing to the low vapour pressure of carbon at these temperatures, rehydrogenation of the deposited carbon does not proceed on lowering the temperature to 200, and practically complete removal of the methane may be effected

The reversibility of the hydrogenation process even in the case of fatty oils, is indicated by a patent to Levey,[3] who claims dehydrogenation of such bodies by subjecting them to the action of a catalytic agent in the vapour phase at temperatures exceeding those under which hydrogenation is accomplished Normann [4] has confirmed this behaviour, which occurs even in the presence of hydrogen although better results are obtained by using a current of another gas, preferably carbon monoxide Normann suggests that these results afford a possible explanation of the difficulty of reducing the iodine number of an oil to zero by catalytic hydrogenation and of the appearance of new unsaturated acids in the oil-hardening process, owing to the addition of hydrogen atoms in one part of the molecule and the splitting-off of others elsewhere [5] Brochet records anomalous results with castor oil,[6] which indicate that the same phenomenon may occur with this oil

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[1] *Ber*, 1923, **56**, 1249 See also Zelinski, *Ber*, 1911, **44**. 3121, 1912 **45**, 3677

[2] *Ber*, 1923, **56** 787, 1716, 1718, 1723

[3] U S P 1374589

[4] *Chem Umschau*, 1923, **30**, 3, *J Soc Chem Ind*, 1923, **42**, 149A

[5] See C W Moore, *J Soc Chem Ind*, 1919, **38**, 320T, Hilditch and C W Moore, *J Soc. Chem Ind*, 1923, **42**, 15T

[6] *Bull Soc. Chim*, 1923, **33**, 626

We have already noted that, in the preparation of formaldehyde from methyl alcohol, the initial stage of the reaction is a process of dehydrogenation:

$$CH_3 . OH \rightleftarrows H . CHO + H_2,$$

but, owing to the fact that all catalysts hitherto employed to bring about this reaction gradually lose their activity, for some cause with no satisfactory explanation as yet, the preparation of formaldehyde has been transformed into a fractional combustion process. The higher alcohols of the aliphatic series, as well as aromatic alcohols, can likewise undergo conversion into aldehydes with elimination of hydrogen in the presence of catalysts, and as such catalytic materials do not appear to lose their activity appreciably even with prolonged running, the technical development of such processes has been possible

The dehydrogenation of primary alcohols is a reversible action:

$$R . CH_2 . OH \rightleftarrows R . CHO + H_2.$$

Hydrogenation of the aldehyde in the presence of reduced nickel proceeds rapidly at 180° in the case of the aliphatic compounds and below 230° for aromatic aldehydes.

Rideal[1] has shown that with ethyl and isopropyl alcohols the dehydrogenation equilibria can be fairly satisfactorily determined at low pressures of the gaseous system, and that the results obtained could be utilised to evaluate the thermal data for the reactions. Thus, for the dehydrogenation of ethyl alcohol a value of ΔH 11,500 cals. was obtained, in fair agreement with data from the heats of combustion of the organic substances.

At high temperatures, however, two other important side reactions proceed with measurable velocity, tending to lower the yield of aldehyde:

(*a*) The formation of saturated hydrocarbons by elimination of CO:

$$R . CHO \rightleftarrows RH + CO$$

Below 300° only small amounts of hydrocarbon are obtained with the aliphatic aldehydes, but the loss due to this reaction is usually somewhat higher in the aromatic series.

(*b*) Dehydration of the alcohol with the formation of unsaturated hydrocarbons:

$$R . CH_2 . CH_2 . OH \rightleftarrows R . CH : CH_2 + H_2O,$$

a reaction which proceeds fairly rapidly at 400° in the presence of catalysts.

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[1] *Proc. Roy. Soc.*, 1921, **99A**, 153.

The employment of metallic catalysts in the preparation of aldehydes.—In the conversion of ethyl alcohol to acetaldehyde metallic copper obtained by reduction of fused copper oxide, gives the most satisfactory results. Formation of aldehyde can already be observed at 200°, but the optimum temperature for operation lies in the neighbourhood of 310° with a permissible latitude of some 20°. At 420° more than 16 per cent of the acetaldehyde is converted into hydrocarbons. With relatively low space velocities (*circa* 200) a 20 per cent conversion can be effected at normal temperatures of operation. The resulting mixture of aldehyde and alcohol vapour mixed with hydrogen and a very small quantity of aldehyde condensation products are passed to a relatively large copper fractionating column whence the alcohol can be recovered and returned to the preheater situate in front of the catalyst tubes. The aldehyde and hydrogen recovered from the middle section and top of the dephlegmating column respectively are practically pure. It is said that the conversion of alcohol into aldehyde by this means is attended with a loss of well below 10 per cent when the due precautions are taken as regards temperature control.

Propyl, butyl, isobutyl, and isoamyl alcohol undergo similar processes of dehydrogenation with formation of the respective aldehydes at temperatures varying between 220° and 300° in the presence of metallic copper. Bouveault[1] cites the dehydrogenation of decyl alcohol, $C_{10}H_{21}$ OH under reduced pressure by similar means.

The most thorough study of the dehydrogenation process at a copper surface with a series of the saturated alcohols has been made by Palmer and his associates.[2] The outstanding result of this work is that, on a given catalyst, the rates of dehydrogenation of the primary alcohols, ethyl, propyl, butyl, isobutyl and isoamyl, are all equal within the limits of experimental error and the temperature coefficient is the same for all. Secondary propyl alcohol reacts with a velocity about five times that of the primary alcohols and has a slightly higher temperature coefficient. The results, taken in conjunction with the probable assumption that the activated layer of molecules is unimolecular, show that these alcohols are adsorbed with the CH_2OH group in contact with the copper surface and the hydrocarbon chains perpendicular to the surface. Constable in the last of the series of these researches, shows that the reaction velocity at 250° C. with ethyl and butyl alcohols was independent of the pressure in the range 10-140 cm. of mercury. It is evident therefore that, in this pressure range, the surface is practically covered with alcohol molecules and the mean life of the molecule in the activated unimolecular layer changes only slowly with the pressure over the range investigated.

The investigation of this reaction has been extended by Sabatier[3] and by Bouveault[1] to secondary alcohols of the aliphatic series as well as to a certain number of aromatic aliphatic derivatives.

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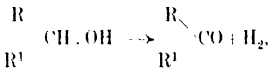
[1] *Bull. Soc. Chim.*, 1908, **4**, 3, 50, 119.

[2] *Proc. Roy. Soc.*, 1920, **98A**, 13; 1921, **99A**, 412; 1922, **101A**, 178; 1924, **106A**, 250; 1925, **107A**, 255, 270, 27.

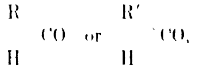
[3] *Ann. Chim. Phys.*, 1905, **8**, 4, 467.

Owing to the fact that the ketones prepared by the dehydrogenation of the secondary alcohols, according to the general reaction



$$\begin{matrix} R \\ & CH.OH \\ R^1 \end{matrix} \longrightarrow \begin{matrix} R \\ & CO + H_2, \\ R^1 \end{matrix}$$

are more stable than the corresponding aldehydes,



$$\begin{matrix} R \\ & CO \\ H \end{matrix} \quad \text{or} \quad \begin{matrix} R' \\ & CO, \\ H \end{matrix}$$

temperatures higher than 300° can usually be adopted, resulting in a more effective conversion of alcohol into ketone by one passage over the copper catalyst. Sabatier states that temperatures up to 400° can be employed with safety, and that a conversion of more than 75 per cent can be effected by this means.

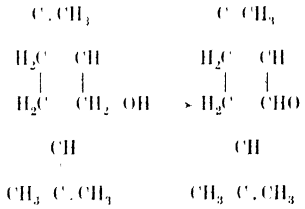
Dehydrogenation of isopropyl alcohol commences at 150°, whilst below 300° the loss due to the formation of propylene is negligible. 2-Butyl and 2-octyl alcohol are comparatively easily dehydrogenated at 300°, whilst the formation of the unsaturated hydrocarbons does not commence to be appreciable until 400°.

Aliphatic alcohols containing a double bond, *e.g.* allyl alcohol, $CH_2:CH.CH_2.OH$, are usually converted into the saturated aldehydes:

$$CH_2:CH.CH_2.OH \rightarrow CH_3.CH_2.CHO,$$

a simultaneous process of dehydrogenation and hydrogenation.

According to Bouveault[2] geraniol is an exception, since citral is practically the only product produced by passage over reduced copper at 200° under reduced pressure:



Geraniol. Citral.

The absence of cymene in the citral, which can be easily formed by the elimination of water and closure of the ring, is under these conditions of dehydrogenation somewhat unexpected. Borneol, likewise, can be converted practically quantitatively into camphor at 300°[1]

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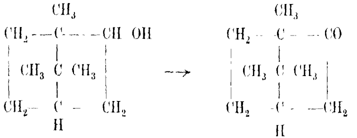
[1] *Bull. Soc. Chim.*, 1906, **3**, 35, 650.

[2] *Loc. cit.*



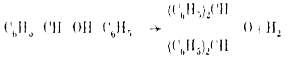
Borneol Camphor

In the presence of metallic copper, benzyl alcohol undergoes partial dehydrogenation at 300°, but at 380° a poor yield of benzaldehyde is obtained, degradation to toluene and benzene taking place simultaneously

The conversion of phenyl ethyl alcohol, on the other hand, into the corresponding aldehyde is easily effected under reduced pressure

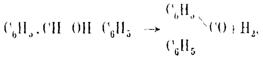
Sabatier and Senderens[2] have investigated the dehydrogenation of the alcoholic derivatives of cyclohexane With cyclohexanol itself, the cyclohexane produced at 300 undergoes but little secondary decomposition, but with the various methyl cyclohexanols by-products such as the unsaturated ring compounds and cresols increase in amount with elevation of the temperature

Knoevenagel and Heckel[3] record an interesting case of ether formation with metallic copper at 280



$$C_6H_5\ CH\ OH\ C_6H_5 \rightarrow \begin{matrix}(C_6H_5)_2CH \\ \\ (C_6H_5)_2CH\end{matrix}\ O + H_2$$

whilst the conversion into benzophenone



$$C_6H_5.CH\ OH\ C_6H_5 \rightarrow \begin{matrix}C_6H_5 \\ \\ C_6H_5\end{matrix}\!\!>CO + H_2,$$

occurs when heated in the absence of copper to 280°-295 Sabatier cites this example as the only exception to the processes of dehydrogenation catalytically accelerated by the presence of reduced copper It is interesting to note that these observers found that the preparation of benzophenone by this process of dehydrogenation could easily be effected in the presence of palladium black Nickel is even more active than copper as a dehydrogenation catalyst Thus, ethyl and he other aliphatic alcohols already undergo appreciable conversion some 50 degrees below that found necessary in the presence of copper Degradation of the aldehyde or ketone produced is, however, as a ule, much more marked, thus limiting the utility of this metal For example, 75 per cent of the propyl aldehyde produced by the dehydrogenation of propyl alcohol at 260° is destroyed during its passage over the catalyst material.

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[1] Goldsmith, B P 17573/1906

[2] *Ann Chim Phys*, 1905, 8, 4, 467.

[3] *Ber*, 1903, 36, 2816

Sabatier and Senderens[1] state that reduced cobalt is intermediary between the last two elements in catalytic activity, whilst platinum and palladium exert an activity similar to that of nickel, although secondary degradation does not proceed to such a great extent. Thus, in the dehydrogenation of ethyl alcohol in the presence of platinum black, although conversion commences at 270° the rapidity of conversion is not marked until a temperature of 370° is reached, when a 75 per cent loss of acetaldehyde is obtained as a result of secondary degradations into methane and carbon:

$$\begin{aligned} C_2H_5.OH &\rightarrow CH_3.CHO + H_2, \\ CH_3.CHO &\rightarrow CH_4 + CO \end{aligned}$$

Experiments with both zinc and brass have given unsatisfactory results, according to Ipatiew,[2] but brass has been used technically for the dehydrogenation of ethyl alcohol.

The use of metallic oxides. In the preparation of formaldehyde from methyl alcohol we have already noted that the use of certain oxides, notably those of aluminium and manganese, as catalytic materials has been attended with definite although somewhat poor yields of the aldehyde.

The extension of the use of certain oxides to the dehydrogenation of the higher alcohols has been made by Sabatier and Mailhe,[3] who arrived at the conclusion that they were less satisfactory than the metals owing to their lower reactivity, thus necessitating the use of higher temperatures with a resulting increase in the secondary formation of hydrocarbons and carbon monoxide. These investigators have classified the oxides investigated into three groups:

(*a*) Those in which the catalytic activity for processes of dehydrogenation is most marked, *e.g.*

$$R.CH_2.OH \rightarrow R.CHO + H_2$$

These include uranium, molybdenum, zinc, and vanadium oxides.

(*b*) Those in which processes of dehydration are accelerated, *e.g.*

$$R.CH_2.CH_2.OH \rightarrow R.CH=CH_2 + H_2O,$$

including non-calcined chromium oxide, silica, and titanium oxide.

(c) Those which accelerated both reactions; including the oxide of glucinum, zirconia, and calcined chromium oxide.

With manganese oxide, dehydrogenation of the aliphatic alcohols does not commence below 360°, at which temperature the conversion is only one-fortieth of that brought about by reduced copper under similar conditions, and secondary decomposition is already quite marked.

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[1] *Ann. Chim. Phys.*, 1905 (viii.), **4**, 473.

[2] Ipatiew, *Ber.*, 1901, **34**, 3579, and 1904, **37**, 2961.

[3] *Ann. Chim. Phys.*, 1910 (viii.), **20**, 313.

Both the oxides of cadmium and tin exhibit interesting phenomena, in that their reactivities at 300° are comparable to those of metals; simultaneous reduction to metal, however, occurs. The metals themselves exhibit marked catalytic activity above their melting points, but owing to the gradual growth of large drops of the liquid metal at the expense of the smaller ones on account of their smaller vapour pressure the active surface of the catalyst is slowly reduced, causing a corresponding reduction in the space time yield for a given size of converter.

THE CRACKING OF OILS

The "cracking" or resolution of hydrocarbons of high boiling point of the aromatic, and more especially of the aliphatic, series into simpler hydrocarbons, both saturated and unsaturated, of relatively low boiling point, is now a well-established industry. In principle the most effective agencies for accomplishing these changes are temperature and pressure, but the influence of catalysts, apart from the specific action of surface contact, both on the velocity of conversion and also on the nature of the product obtained is so marked that their industrial significance is now a matter of importance. At the same time, a study of their behaviour, although not throwing much light on the nature of the catalytic processes involved, is giving valuable information as to the methods of formation of the various products in the pyrogenetic decomposition.

To Murdock (1792) must be given the credit for the observation that the effect of heat on heavy oil was to produce a gas suitable for illumination. Since that time the cracking of heavy oils has been stimulated by the following factors: (i.) the relative increase in output of very heavy oils over paraffin, petrol, and natural gas owing to the increased rate of consumption of the latter; (ii.) the increased demand for petrols and petrol ethers as fuels for internal combustion engines and solvents, for paraffin in the stationary power engines of small sizes and for illumination, and for aromatic hydrocarbons as raw materials in the chemical industries.

The primary decomposition of an aliphatic hydrocarbon into its simpler constituents prior to the rearrangement by synthesis of these decomposition products into open- or closed-chain hydrocarbons is the explanation of the "cracking" process now generally adopted. All evidence[1] points to the hypothesis that catalysts exert a considerable activity in the decomposition of the original hydrocarbon and may exert a marked influence in the secondary synthesis. Since, in general, degradation and synthesis in the reactions cannot be separated, the exact functions of the catalysts employed must be considered at present as merely speculative in character.

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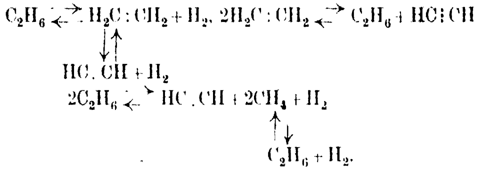
[1] See the carefully compiled literature by Lomax, Dunstan, and Thole, *J. Inst. Pet. Tech.*, 1916, **3**, 9, 36, 120.

Two alternative theories have been advanced to interpret the mechanism of the first or disintegrating stage of the cracking process, that of Berthelot[1] and the more recent one of Bone and Coward[2]

According to Berthelot disruption proceeds in stages with the primary elimination of hydrogen, with or without the simultaneous formation of methane and the production of an olefinic hydrocarbon containing one or more double bonds. Thus, ethane may be considered to undergo the following alternative or simultaneous pyrogenetic decompositions:



$$\begin{tikzcd}[column sep=small]
C_2H_6 \arrow[r, shift left] & H_2C:CH_2+H_2, \arrow[l, shift left] \arrow[d, shift right] & 2H_2C:CH_2 \arrow[r, shift left] & C_2H_6+HC\vdots CH \arrow[l, shift left] \\
 & HC.CH+H_2 \arrow[u, shift right] & & \\
2C_2H_6 \arrow[r, shift left] & HC.CH+2CH_4+H_2 \arrow[l, shift left] \arrow[d, shift left] & & \\
 & C_2H_6+H_2. \arrow[u, shift left] & &
\end{tikzcd}$$

The intermediary formation of olefines as well as of di- and tri olefines during the thermal decomposition of a paraffin is a well-known phenomenon, having been confirmed by the researches of Thorpe and Young,[3] Haber,[4] and others. It is, furthermore, a matter of great technical importance in the preparation of motor spirits, since, on storage, especially under the influence of light, the di- and triolefines polymerise to form a gummy residue capable of making the inlet valves of internal combustion engines faulty in their action. Mono-olefines or chain hydrocarbons with only one double bond do not appear to possess these objectionable characters to such a high degree, and may be left in the spirit. This consideration should be noted, since the olefinic constituent of a cracked petrol is a high one, and complete removal would entail a heavy loss both in spirit and in sulphuric acid. Fractional removal of the di- and triolefines can be accomplished by scrubbing with 1 to 2 per cent of sulphuric acid.

Possible hydrogenation in solution by a catalytic process or in the vapour state at a low temperature suggests itself as a promising alternative.

Bone and Coward, on the other hand, advanced the nascent radical theory. On this view the hydrocarbon is considered to be at least momentarily split up into radicals, $\equiv CH$, $= CH_2$, and $- CH_3$, having a fugitive existence and undergoing immediate polymerisation to more

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[1] *Compt. rend.*, 1866, **62**, 905; **63**, 788; and *Bull. Soc. Chim.*, 1867 (ii.), **7**, 251.

[2] *J. Chem. Soc.*, 1908, **93**, 1197.

[3] *Proc. Roy Soc.*, 1871, **19**, 370.

[4] *J. f. Gasbeleucht.*, 1895, **39**, 377-830; *Ber.*, 1896, **29**, 2691.

complex hydrocarbons, usually, however, simpler than the original raw material

The formation of a double bond is an endothermic reaction, the first stage of the cracking process thus requiring the continuous supply of a considerable amount of energy, in a paraffinoid hydrocarbon amounting to approximately 30,000 cals per grm -mol

Rittman[1] has calculated the velocity constants of the typical cracking reaction, $C_2H_6 \rightarrow C_2H_4 + H_2$, at various temperatures with the following results

k_{500} 0.027
k_{750} 0.071,
k_{900} 1.28

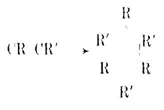
Thus, the rate of double bond formation or commencement of the cracking process of ethane is already quite appreciable at 600

The formation of a diolefine may be the result of the further elimination of hydrogen from a mono-olefine, or, according to Ostromisslenski,[2] due to thermal decomposition with the liberation of a paraffin hydrocarbon thus

$$CH_2\,CH\,CH_2\,CH_2\,R \longrightarrow CH_2\,CH\,CH\,CH_2 + RH$$

Thus far, we have shown how in the simple cracking process the production of gases, such as methane, hydrogen, the lower paraffin hydrocarbons, and the olefines, can be accounted for Such products are usually obtained in the cracking of paraffin up to 600 , whilst, according to Rittman,[3] petrol formation may already be obtained at as low a temperature as 400

The formation of ring compounds. According to Berthelot the formation of acetylene is possible in the process of degradation of a paraffin under the influence of temperature and pressure with or without a dehydrogenating catalyst Although the presence of acetylene has never actually been proved, it may be argued that almost instantaneous polymerisation to ring compounds takes place at the cracking temperature, thus



According to Bone and Coward similar results would be obtained by the rapid polymerisation of the nascent radical CH

It must not be forgotten, however, that the formation of stable ring compounds is also possible through the condensation of olefines or dehydrogenation of a triolefine. We have already noted that the formation of polyolefines is possible in a cracking process, and our knowledge of the extraordinary reactivity of the system of conjugated double bonds:

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[1] *J Ind Eng Chem*, 1915 **6**, 1029, **7** 945, 1916, **8**, 20
[2] *J Russ Phys Chem Soc*, 1910, **42**, 145, 1915 **47**, 1947
[3] *J Ind Eng Chem*, 1915 and 1916, **7**, 1019

$$.C:C.C:C.,$$

would lead us to suppose that cyclic condensation would probably proceed via a polyolefinic compound, and not through the hypothetical intermediary formation of acetylene or of the still more nascent radical $\equiv CH$. Ipatiew[1] has shown the formation of cyclohexane from *n*-heptane via *α* : *n*-hexylene, and Lebedev[2] the formation of the same compound from erythrene.

Cyclic polymethylenes and aromatic hydrocarbons may thus result from processes of polymerisation of olefines, diolefines, and acetylenes, or by the formation of closed rings from open chains by a process of dehydrogenation.

Since, whichever view be adopted, degradation has to proceed further than in the preparation of petrols before the formation of cyclic compounds is possible, we would expect larger yields at higher cracking temperatures and especially in the presence of dehydrogenating catalysts. The optimum temperature for aromatic hydrocarbons in practice is stated by Rittman to be between 650° and 700°. For Baku petroleum, Smolenski, Turowicz, and Dobrowlski[3] report temperatures of 680°-720° C., benzene, toluene, xylene, anthracene, and naphthalene are among the products. Above 800° thermal degradation to carbon and hydrogen commences to be a source of trouble and hydrocarbon loss, partly due to the ultimate dissociation of methane, $CH_4 \rightleftarrows 2H_2 + C$, which is practically complete under 1 atmosphere pressure at 1200°.

It must not be forgotten that, owing to the complex composition of the natural oil before cracking, the resulting product, when cracked at any given temperature and pressure of operation, will also be complex. Thus, the presence of ring compounds when petrol is desired or vice versa, or the occurrence of a carbon deposition in the retorts, stills, or steel tubes, can scarcely be avoided.

For the general effect of temperature and pressure on cracking processes, as well as the relative advantages of cracking in the vapour or liquid state, the reader is referred to the papers by Lomax, Dunstan, and Thole cited above.

Dehydrogenation of cyclic compounds. Sabatier and Senderens[4] showed that cyclohexane at a temperature of 270°-280° in the presence of nickel underwent a process of dehydrogenation with the formation of benzene and methane:

$$3C_6H_{12} \longrightarrow 2C_6H_6 + 6CH_4.$$

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[1] *Ber.*, 1913, **46**, 1748.

[2] *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249.

[3] *J. Soc. Chem. Ind.*, 1922, **41**, 402A.

[4] *Compt. rend.*, 1897, **174**, 616.

substituted cyclohexanes and hydronaphthalenes behave in a similar fashion Reduced copper is slightly less active,[1] dehydrogenation of cyclohexane commencing only at 300°.

The experiments of Cobb and his associates at Leeds University[2] on the reactions occurring among benzene and its homologues when submitted to conditions similar to those obtaining during the carbonisation of coal, are of interest also from the point of view of dehydrogenation, and demonstrate the operation of such reactions in the destructive distillation of coal

Cobb demonstrated that in a stream of nitrogen rich in benzene decomposition sets in at temperatures in the neighbourhood of 550° A solid product, diphenyl, is one of the products of decomposition and results manifestly from a dehydrogenation process according to the reaction

$$C_6H_6 \longrightarrow C_6H_5\ \ C_6H_5 + H_2$$

With increasing temperature an increased yield of diphenyl is obtained, but, at more elevated temperatures, further decomposition sets in, a three-ring compound diphenyl benzene being produced

It was demonstrated that the atmosphere in which the reaction was conducted had a decisive influence on the decomposition process Thus, with hydrogen in lieu of nitrogen as diluent, the formation of diphenyl was reduced, with a sufficient excess of hydrogen the decomposition of benzene was practically suppressed an observation which explains the stability of benzene in the processes of coal carbonisation

With toluene in nitrogen similar results were obtained At 600° the two-ring compound stilbene ($C_{11}H_{12}$) was produced In a hydrogen atmosphere, however, hydrogenation of the molecule arose with production of methane and benzene Xylene behaved in a similar manner.

It may be mentioned that substituted hydrogenated ring compounds behave in a similar manner Thus piperidine was shown by Ciamician[3] to undergo dehydrogenation over nickel, between 180° and 250°, to pyridine.

Palladium black is even more active than nickel, thus, with cyclohexane, dehydrogenation commences at 170° and proceeds smoothly at 200° At lower temperatures, viz 100°-110°, hydrogenation of benzene occurs

Dehydrogenation of open-chain hydrocarbons.—Between 350° and 400° the aliphatic saturated hydrocarbons are dehydrogenated in the presence of reduced nickel, thus pentane is finally converted into carbon and hydrogen, although the intermediary products, propane, ethane, and methane, can be isolated.

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[1] Sabatier and Mailhe, *Compt. rend*, 1903, **137**, 240

[2] See Wm Young Memorial Lecture, Glasgow, Sept 1918

[3] *Atti R Accad Lincei*, 1907, **16**, 808

The unsaturated olefine hydrocarbons undergo similar decomposition, but part of the olefine at the same time becomes saturated. Thus, in the presence of reduced nickel at 300°, ethylene is converted into a mixture of ethane, methane, carbon, and hydrogen.

With cobalt, dehydrogenation commences at 300°, with iron at 350°, whilst platinum and copper exert no catalytic activity below 400°.

Acetylene, as is well known, undergoes dehydrogenation and partial polymerisation at very low temperatures. Thus, in the case of platinum black, the reactivity is already quite marked at 150°. Ferrum reductum is raised to the point of incandescence when exposed to acetylene, with the simultaneous production of soot. After a short period the reaction velocity becomes slower and partial polymerisation and hydrogenation of the acetylene occur.

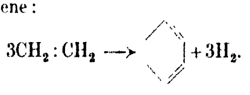
Copper at 180° absorbs acetylene very readily, the product being a brownish-yellow modification containing a hydrocarbon cuprene, $(C_7H_6)_n$.[1] According to Sabatier the formation of cuprene is the result of the interaction of a carbide of copper produced by the dehydrogenation of acetylene with fresh acetylene, the copper being thus decarbonised, and able, therefore, to renew its catalytic functions.

Small quantities of cuprene can also be obtained with reduced nickel in the presence of acetylene at 180°.

The formation of cyclic compounds by dehydrogenation. This process of dehydrogenation is a very usual one in organic chemistry, and owing to the ease with which six carbon atom ring compounds are formed by loss of hydrogen from open chains, has led to the synthesis of aromatic compounds of high complexity.

Aluminium chloride is the most effective catalyst for such processes of dehydrogenation, the velocity of dehydrogenation being frequently already appreciable at 80° and vigorous at 180°. In common with other pyrogenetic reactions, simple passage through a red-hot tube will accomplish the same ends, but the yield is usually much smaller owing to the process of degradation proceeding further at such elevated temperatures. Reduced nickel is also an active catalytic material, but the necessary temperatures to be maintained are usually considerably higher than with aluminium chloride.

As typical syntheses, the following may be mentioned, showing the gradual formation of polycyclic compounds of high complexity. Ethylene yields benzene:



The researches of Ipatiew and Aschan[2] showed that polymerisation and dehydrogenation would proceed rapidly at 275° in the presence of aluminum or zinc chloride Dibenzyl is rapidly converted in phenanthrene and α-ethyl naphthalene into acenaphthene by passag through a red-hot tube

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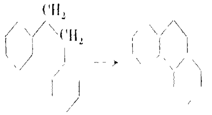
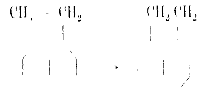
[1] Sabatier and Senderens, *Bull. Soc. Chim.*, 1899, 21, 530.

[2] *Loc. cit.*

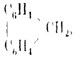


Dibenzyl Phenanthrene



α Ethyl naphthalene Acenaphthene

The synthesis of fluorene,



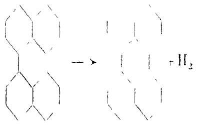
$$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} \!\!> CH_2,$$

chrysene,

and picene,

can be brought about in a similar manner

Scholl and his co workers[1] have paid special attention to the use of aluminum chloride in the formation of polycyclic derivatives of naphthalene and anthracene Thus, dinaphthalene is easily converted into perylene



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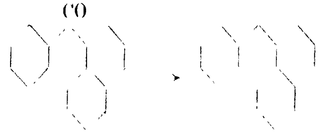
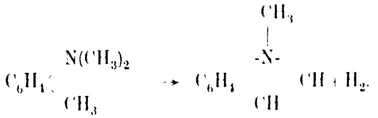
[1] *Ber.*, 1910, **43**, 1737, 2203, *Annalen*, 1912 **394**, 111

In a similar manner phenyl α-ketonaphthalene can be dehydrogenated at 140° to produce benzanthrone :



Catalytic processes of dehydrogenation can also be applied to the formation of heterocyclic compounds. Carrasco and Padya [1] showed that dimethyl *o*-toluidine in the presence of reduced nickel at 300° was partly converted into methane, toluidine, and methyltoluidine, more than 24 per cent of methylindol being, however, simultaneously produced :



$$C_6H_4\left\langle\begin{array}{l}N(CH_3)_2\\ \\ CH_3\end{array}\right. \rightarrow C_6H_4\begin{array}{c}CH_3\\ |\\ -N-\\ \\ CH\end{array}CH + H_2.$$

Methyl *o*-toluidine with similar treatment yields a small quantity (6 per cent) of indol

Use of metals in cracking processes. In 1866 Berthelot noted the catalytic decomposition of acetylene to carbon and hydrogen in the presence of finely divided iron

Moissan and Moureau [2] confirmed Berthelot's results and showed that cobalt, and especially nickel, when freshly prepared, exhibited similar marked activity.

In 1910 Ostromisslenski [3] showed that crude Russian petroleum, when passed over reduced nickel at 600°-700°, was completely disintegrated to hydrogen, methane, and a carbonaceous residue. Ubblehode,[4] working at 350°, showed that the cracking process had already commenced to produce lighter distillates at a temperature some 100° lower than would be necessary in the absence of any catalytic material [5] Zanetti [6] conclusively showed from experiments on propane and butane that nickel was an effective catalytic material in the preparation of petrols, but not for the formation of aromatic substances. These observations form the basis of several patents.[7] Several patents have likewise been taken out for the use of nickel as a catalyst, for a mixture of petroleum vapour and hydrogen, so that cracking of the oil with simultaneous saturation of the olefines would take place.[8] It is, of course, unlikely that any process of secondary saturation would occur at the elevated temperatures, 350°-450°, necessary for the cracking process itself.

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[1] *Gazzetta*, 1907, **37**, 12149.

[2] *Compt rend.*, 1896, **122**, 1241.

[3] *J. Russ. Phys Chem Soc*, 1910, **42**, 195

[4] *Petroleum Zeit*, 1912 (vii.), **9**, 334, 1233, 1911.

[5] See Lamplough, B.P. 19702 1912.

[6] *J Ind. Eng Chem*, 1916, **8**, 674

[7] Hall, B.P. 17121/1913, Higgins and Preston, B P. 23876 1914, and others

[8] Phillips and Buttell, B.P. 23977/1907 ; Planes, Ltd, B P. 5245/1913.

The experiments of Ipatiew, Engler, Kuznetzov, and others showed that copper, iron, or aluminium showed no advantages over nickel as catalytic agents. We may conclude that the use of reduced metals, especially nickel, in cracking processes is of some material advantage, when petrol is the desired product; in the presence of such a catalyst, the cracking temperature is appreciably lower, the formation of aromatic compounds practically eliminated, and the olefine content of the finished spirit may be slightly reduced by secondary hydrogenation. Technical difficulties, such as the deposition of carbon on the surface of the catalyst, must, however, be expected.

Use of metallic oxides in cracking processes.—Alumina[1] and titanium dioxide[2] exert a slight catalytic activity at 350°, paraffins being partly dehydrogenated at this temperature, whilst at higher temperatures the yield of aromatic compounds is sensibly increased by the presence of such catalytic oxides. Hirschberg[3] claimed an extraordinary activity for chromium oxide prepared by the ignition of ammonium bichromate.

Ipatiew was able to isolate various aromatic hydrocarbons from the residues obtained by the passage of ethylene over alumina at 380°-400 under 70 atmospheres pressure. In the absence of alumina, cyclic paraffins and olefines only were obtained. Similar results were obtained by this investigator with cyclohexane at 500 under high pressures. With *n*-hexane at 650° under normal pressures no aromatic substances were obtained.

It may be concluded that the use of the oxides of aluminium, titanium, and chromium might be of slight service where a high yield of aromatic hydrocarbons is desired and the cracking process is conducted under elevated pressures.

The Friedel and Crafts reaction where the halides of certain elements, especially aluminium, are used as catalytic agents, form the basis of several patents on cracking processes.[4]

It is claimed that "heavy" petroleum is readily converted into aromatic hydrocarbons whilst the polymerisation of the olefines proceeds rapidly in the presence of the halides of aluminium and zinc.

At high temperatures, *circa* 1000°, methane and the simple olefines only result,[5] whilst at very low temperatures polymerisation to cycloparaffins occurs. Ipatiew obtained a good yield of naphthalenes at

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[1] Ubbelohde, *loc. cit.*

[2] Zelinski, *J. Russ. Phys. Chem. Soc.*, 1915, **48**, 610.

[3] B.P. 1414/4573, 1905.

[4] Athel, B.P. 4764/1877; B.P. 7112/1913; B.P. 17838/1913, and especially McAfee, B.P. 22243/1914; U.S.P. 1127465/1915; also *J. Ind. Eng. Chem.*, 1915, **7**, 737.

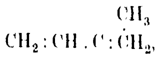
[5] Gustavson, *J. Russ. Phys. Chem. Soc.*, 1881, **13**, 1149.

375°, from ethylene at 70 atmospheres pressure in the presence of zinc chloride; aluminium chloride was even more active.

ISOPRENE

In view of the importance of the possible technical development of a process for producing rubbers and even terpenes such as camphor from coal tar, shale, or crude oils, it may be mentioned that the simplest hydrocarbon which offers a reasonable opportunity for an economic synthesis of these substances is hemiterpene or isoprene (methyl divinyl), C_5H_8, or one of its simple derivatives.

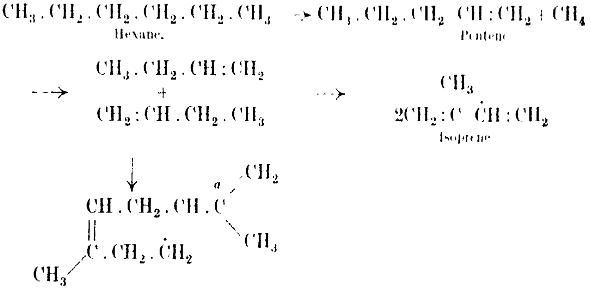
Isoprene contains two ethylene linkages:



$$CH_2 : CH . \overset{CH_3}{C} : CH_2,$$

and is present in fairly large quantities in the distillate obtained by the destructive distillation of rubber or the decomposition, by heat, of terpenes.

Ostromisslenski[1] has already shown that dipentene and dihexene produced by dehydrogenation of pentane and hexane or the elimination of methane from hexane and heptane, with subsequent polymerisation of the olefine when heated to 500°, give appreciable quantities of isoprene and dimethyl divinyl. We may thus consider that the first steps in the synthesis of isoprene are as follows:



$$\underset{\text{Hexane.}}{CH_3 . CH_2 . CH_2 . CH_2 . CH_2 . CH_3} \rightarrow \underset{\text{Pentene}}{CH_3 . CH_2 . CH_2 . CH : CH_2} + CH_4$$

$$\dashrightarrow \begin{matrix} CH_3 . CH_2 . CH : CH_2 \\ + \\ CH_2 : CH . CH_2 . CH_3 \end{matrix} \dashrightarrow \underset{\text{Isoprene}}{2CH_2 : \overset{CH_3}{C} . CH : CH_2}$$

Dipentene

The double bonds in the α, ϵ position show their usual tendency to form a conjugated system with rupture of the molecule to take up the α, γ positions.

According to Berthelot isoprene and similar derivatives of divinyl do not appear to result from the decomposition of a paraffin, but through the intermediate formation of a complex triolefine. Ostro-

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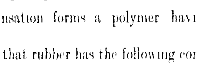
[1] *J. Russ. Phys. Chem. Soc.*, 1905, 47, 703 *et seq.*

missleuski postulated the formation of a simple olefine which would then break down at 500° to form divinyl

$$CH_2 \; CH.CH_2 \; CH_2 \; R \rightarrow CH_2 \; CH \; CH \; CH_2 + RH$$

Isoprene on condensation forms a polymer having a rubber-like consistency

Harries suggests that rubber has the following constitution



$$\left| \begin{matrix} CH_3 \; C \; CH_2 \; CH_2 \; CH & \\ & HC \; CH_2 \; CH_2 \; C \; CH_3 \end{matrix} \right|,$$

a simple polymer of isoprene

The catalysts employed in the polymerisation of isoprene to rubber.—Greville Williams[1] was the first to observe that a rubber like compound could be obtained by the dry distillation of isoprene which had been allowed to stand exposed to the air Bouchardat[2] obtained " a substance analogous to natural caoutchouc " by the action of concentrated hydrochloric acid, five times the weight of the isoprene employed, contained in sealed glass tubes for several weeks

Three years later Tilden[3] noted that nitrosyl chloride was as effective as hydrochloric acid in accelerating the polymerisation of isoprene The same investigator noted[4] the polymerisation through the agency of time and light, and showed that the polymerisation product possessed many of the properties of natural caoutchouc, even to the action of sulphur effecting vulcanisation

Kondakow[5] effected the polymerisation of dimethyl 2 3-butadiene-1 3, a homologue of isoprene to a rubber by subjecting it to the action of alcoholic potash for three days

Lebedev,[6] utilising daylight, Ostromisslenski and Koch[7] with ultra-violet radiation, and Collie,[8] with the silent electric discharge, all effected the complete and relatively rapid conversion of isoprene into rubber, this being superior to all chemical catalysts thus far investigated, with the possible exception, perhaps of oxygen or ozonised air when relatively large quantities of simple polymers usually the dimeride and trimeride, are generally obtained

With the increase in the price of rubber subsequent to 1906, the problem of rapidly effecting the complete polymerisation of isoprene was attacked with renewed vigour Harries, in 1910 showed that heating to 90 -100° in a sealed tube with acetic acid for eight days effected the conversion, but the yield of rubber was extremely variable Hoffmann and Coutelle,[9] of the Bayer firm, made the important observation that pure isoprene or its isomers rapidly polymerises to caoutchouc with good yields when subjected to heat, either in the presence of or without catalytic agents. Previous attempts at thermal polymerisation were unsuccessful, doubtless due to the presence of impurities. Matthews, in 1910,[1] showed that metallic sodium was a polymerising catalyst of unique activity. According to Harries[2] butadiene is converted at the ordinary temperature in a few hours; isoprene is converted at about 60 almost quantitatively into caoutchouc without the formation of any dimerides in from fifty to one hundred hours, whilst the sodium for the greater part is unaltered.

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[1] *Phil Trans* 1860 **150** 254

[2] *Bull Soc Chim*, 1875, **80** 1446, *Compt rend* 1879, **89** 361

[3] *Chem News*, 1882, **44**, 170

[4] *Ibid*, 1892 **65** 265

[5] *J pr Chem*, 1901, **64** 109

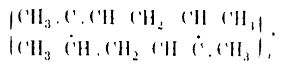
[6] *J Russ Soc*, 1909, **41** 1868

[7] *Chem Zeitsch* 1912, **36**, 150

[8] *J Chem Soc*, 1905, **87**, 1540

[9] F P 414382, 1909

Sodium-condensed caoutchouc is, however, of different structure from that obtained by polymerisation by heat or with the aid of acetic acid, and probably has the following structure proposed by Harries:



$$\left|\begin{array}{l}CH_3.C.CH\ CH_2\ CH\ CH_3\\ CH_3\ \dot{C}H.CH_2\ CH\ \dot{C}.CH_3\end{array}\right|.$$

Various other catalytic agents have been proposed from time to time, such as acetic anhydride,[3] cerium or vanadium salts,[4] and sodamide,[5] but do not appear comparable in activity with either acetic acid or metallic sodium as condensing agents.

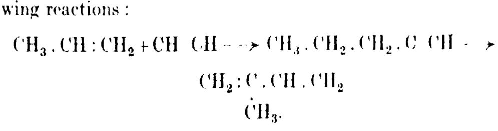
Mention may be made of an interesting series of catalytic reactions proposed by De Boistesselin and Dubose,[6] in which methane and acetylene are used as raw materials. It is proposed to pass methane over carbon deposited on copper oxide at 400-450, when, it is stated, ethylene is obtained together with some of the higher olefines:

$$CH_4 + 3C \longrightarrow 2C_2H_2$$

Dubose states that the proportions actually obtained were

Ethylene .	36 per cent
Butylene . . .	42 ,,
Higher olefines and hydrogen	21 ,,

If butylene and acetylene in equivalent proportions be passed over animal charcoal heated to 150, isoprene is produced according to the following reactions:



$$CH_3.CH:CH_2 + CH\ CH \dashrightarrow CH_3.CH_2.CH_2.C\ CH \dashrightarrow \begin{array}{l}CH_2:C.CH.CH_2\\ \qquad\ \ \dot{C}H_3.\end{array}$$

Ethylene, in a similar manner, can be converted into isoprene by interaction with acetylene followed by subsequent methylation with methyl chloride

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[1] F P. 437547 1910; B P. 24790/1910.

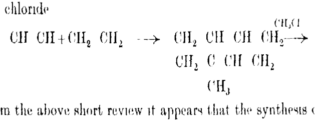
[2] *Annalen*, 1911, **383**, 157.

[3] F P. 433825/1910.

[4] F P. 440173/1910.

[5] B.P. 9219/1910.

[6] *Rubber, its Production, Chemistry, and Synthesis* (Griffin, 1918).



$$\mathrm{CH\ CH + CH_2\ CH_2 \longrightarrow CH_2\ CH\ CH\ CH_2 \xrightarrow{CH_3Cl}}$$
$$\mathrm{CH_2\ \underset{\displaystyle CH_3}{C}\ CH\ CH_2}$$

From the above short review it appears that the synthesis of many derivatives of the terpenes as well as of the rubbers from simple oils or tars, through the intermediary of divinyl and its derivatives, is by no means an insoluble problem

Simultaneous hydrogenation and dehydrogenation —Since one and the same catalyst can effect both hydrogenation and dehydrogenation it ought to be possible to combine the two processes in one operation, the hydrogen for the one process being produced by the other process It is evident, from the discussion which has already preceded, that success in such transfer will involve a choice of reactions such that hydrogenation is possible in the one case at a temperature at which dehydrogenation will occur in the other There are several examples of such a combination and the list could doubtless be readily extended

Zelinski and Glinka[1] treated methyl tetrahydroterephthalate with palladium and obtained the terephthalate and the hexahydroterephthalate

Boeseken[2] studied a similar case He passed dihydrobenzene and also tetrahydrobenzene over nickel at 180° C He also sealed up the latter hydrocarbon with palladium In every case he obtained a mixture of benzene and cyclohexane Zelinski[3] has recently recorded the same experiment and calls the process an "irreversible" catalysis The "irreversibility" lies in the number of the processes involved

Meyer and Eckert[1] mention the dehydrogenation of ethyl alcohol to aldehyde and the addition of hydrogen to benzoquinone or to thymoquinone under the influence of light Armstrong and Hilditch[5] transformed cyclohexanol by the action of nickel into cyclohexanone and methyl phenyl propionate Padoa and Foresti[6] made a quantitative study of the transfer of hydrogen from isopropyl alcohol to diethyl ketone and to benzene with the formation of diethyl carbinol and cyclohexane respectively. They found equilibria corresponding to those calculated from the Nernst heat theorem Sabatier and Murat[7] passed the vapours of alcohols with benzaldehyde, benzophenone, benzyl alcohol, and acetophenone over thoria at 420° C, and got complete reduction to toluene, ethyl benzene, and diphenyl methane Kayser[8] has patented the hydrogenation of an unsaturated oil by heating it with borneol or isoborneol in presence of nickel To this list of examples Milligan and Reid[1] have added the transference of hydrogen from an alcohol to an aldehyde. At 300°-380° C. over ceria, ethyl alcohol gives up its hydrogen to the vapours of aldehydes simultaneously passed over the catalyst. In this way benzyl, phenyl ethyl, and heptyl alcohols and citronellol have been prepared. Fouling of the catalyst caused its life to be short. Condensation of the aldehydes is probably responsible for this.

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[1] *Ber*, 1911, **44**, 2305

[2] *Rec trav chim*, 1918, **37** 255

[3] *Ber*, 1924, **57**

[4] *Monatsh*, 1918 **39**, 241

[5] *Proc Roy Soc*, 1917, **96**A, 322

[6] *Atti R Accad Lincei*, 1914, **23** (ii), 84

[7] *Compt rend*, 1913, **157**, 1499, *Bull. Soc Chim*, 1914, **15**, 227

[8] U S P 1134746

Mixed dehydrogenation.—An example of dehydrogenation in which the hydrogen comes from two substances simultaneously is provided by the synthesis of amines from aromatic hydrocarbons and ammonia. Thus, benzene and ammonia led through a heated tube yield a trace of aniline:

$$C_6H_6 + NH_3 = C_6H_5NH_2 + H_2.$$

Meyer and Tanzen[2] attempted to make this a practicable synthesis by using a nickel catalyst at 550° C. Again no more than a trace of amine was obtained. It can be readily shown by thermodynamic calculation that this is because the equilibrium is exceedingly unfavourable. Rowe[3] claimed the production of naphthylamine from naphthalene and ammonia, in 2 per cent yield, with a nickel catalyst at 300° C. Recent efforts to repeat this result did not lead to success.

Starting with acetylene, a reaction involving a dehydrogenation has also been reported. Acetylene and ammonia when passed over contact agents, for example, bauxite, at 350°-380° C., yield acetonitrile and hydrogen:

$$C_2H_2 + NH_3 = CH_3CN + H_2\,^{4}$$

[1] *J. Amer. Chem. Soc.*, 1922, **44**, 202.

[2] *Ber.*, 1913, **46**, 3181.

[3] *J. Soc. Chem. Ind.*, 1920, **39**, 244T.

[4] Cf. D.R.P. 368176.

CHAPTER X

CATALYSIS IN NITROGEN FIXATION

The phenomenon of catalytic action is to be observed in all the technical methods employed for the fixation of atmospheric nitrogen. Whilst some methods, such as the synthetic production of ammonia from its elements or the direct formation of cyanides, are dependent for their success on the activity of particular catalysts, the efficiency of other processes may be impaired, such as the arc method of producing nitric acid, or greatly augmented, as in the manufacture of cyanamide by the presence of catalytic agents.

In the arc process developed by Pauling the arc is struck between horn-shaped iron electrodes. The arc is blown upwards between the horns by a powerful blast of air. At the tips of the horn the arc breaks and starts anew at the base. Rossi on examination of the method found that the yields obtained were lower than those in the Birkeland-Eyde or Schonherr processes, and noted that small particles of iron oxide were ejected from the electrode surfaces by the air blast. The iron oxide was found to accelerate the decomposition of nitric oxide at temperatures below that at which a “ frozen ” equilibrium is normally obtained. By replacement of the iron electrodes by water-cooled aluminium horns this difficulty was eliminated.

The nitric oxide formed in the arc process undergoes oxidation with the excess oxygen present in the air to the dioxide, which can be removed by water-scrubbing. If relatively concentrated nitric acid be desired, the problem of accelerating the relatively slow rate of oxidation of the nitric oxide arises. This reaction is termolecular in character according to the reaction

$$O_2 + 2NO \dashrightarrow 2NO_2$$

Whilst small traces of bromine and chlorine are said to act as effective catalysts the reactions are involved and do not appear to have been studied in detail. Burdick[1] found that the reaction velocity was capable of marked acceleration at surfaces. The relative velocities at surfaces of steamed coke, charcoal, and glass are of the order

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[1] *J. Amer. Chem. Soc.*, 1922, **44**, 245.

Coke, 300,
Charcoal, 10,000,
Glass, 18-20.

SYNTHETIC AMMONIA

The technical production of pure ammonia by the catalytic combination of nitrogen and hydrogen must be considered as one of the greatest triumphs of modern physical and engineering chemistry.

In 1865 Deville[1] observed that the decomposition of ammonia under the influence of a spark discharge was never complete, thus indicating the reversibility of the reaction:

$$2NH_3 \rightleftarrows N_2 + 3H_2$$

The communication of Prof. C. Matignon to the inaugural session of the Société de Chimie Industrielle presents a very great interest to all concerned in ammonia synthesis in particular, and also in the application of science to industry in general. The communication records a research into the scientific literature and more especially the patent literature concerning the production of ammonia from its elements.

A résumé of the patents as set forth by M. Matignon may be given. Dufresne, in 1865, took out a British patent,[2] in the name of Charles Tellier, for the preparation of oxygen. In the patent it is stated that "a large quantity of nitrogen is liberated in these operations. To utilise this gas, I pass it over spongy iron heated to redness and which absorbs nitrogen. In this state I then pass hydrogen over the combination of iron and nitrogen thus formed. Decomposition is immediate and the great quantity of ammonia thus produced lowers the price of oxygen."

Tessié du Motay[3] took out a patent for a continuous process of ammonia synthesis. The production of ammonia was to be effected by passage of hydrogen and nitrogen alternately over tubes containing the nitrides of titanium heated to redness. The nitrides Ti_3N_2 and TiN, heated with hydrogen, yield ammonia and the nitride Ti_5N_3, which is reconverted by nitrogen to TiN and Ti_3N_2.

Charles Tellier[4] proposed to unite nitrogen and hydrogen by alternate passage over heated iron. Spongy iron is recommended, the two gases to be obtained by the respective actions of steam and air on zinc.

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[1] *Compt. rend.*, 1865, 60, 317.

[2] No. 1833.

[3] F.P. 92346/1871.

[4] F.P. 138472/1881.

The patents of the Société Azote de Paris represented by Charles Tellier[1] embody the following claims (1) The preparation of nitrogen and hydrogen by the respective action of air and steam upon zinc (2) The alternate passage of nitrogen and hydrogen through heated vessels filled with spongy titaniferous iron to produce ammonia (3) The employment of pressure up to 10 atmospheres, using heated vessels containing platinum deposited on pumice or charcoal (4) The use of titaniferous iron admixed with another metal

Ramsay and Young, in 1884, recorded the formation of small quantities of ammonia by passage of nitrogen and hydrogen over heated iron wires

An Austrian patent of Hlavati[2] claimed the synthesis of ammonia by passage of hydrogen and nitrogen through a heated chamber containing as catalyst a mixture of titanium or titaniferous bodies in admixture with platinum supported on porous materials

A Norwegian company Christiania Minekompanie, took out the French patent No 225183/1896 with several important claims Nitrogen and hydrogen were to be passed through heated vessels containing titanium precipitated in a finely divided condition on neutral supports, with or without the addition to the titanium of platinum or the platinum metals, further, the titanium could be replaced by bismuth, antimony, or alkali or alkaline earth metals, but in such cases platinum and the platinum metals were to be employed

In 1901 Le Chatelier patented[3] the direct combination of hydrogen and nitrogen, in which he specially claims the use of high pressures up to 100 atmospheres in order to facilitate combination coupled with the use of appropriate catalytic material

Perman noted the activity of reduced iron copper zinc, cobalt, nickel, palladium, etc in promoting the combination of nitrogen and hydrogen and showed also the advantage of pressure

In 1904 the subject was again taken up by Haber and his co-workers, especially Van Oordt and Le Rossignol,[4] and was carried to the stage of a complete technical success by the Badische Anilin- und Soda-Fabrik at Oppau

Haber at first investigated the equilibrium conditions obtaining between a mixture of nitrogen, hydrogen and ammonia at varying temperatures Equilibrium was obtained by the passage of nitrogen and hydrogen over various catalytic materials and was also arrived at from the other side by the decomposition of ammonia As catalytic materials, iron, nickel, chromium, and manganese were used at temperatures ranging between 700° and 1000°

The most recent determinations of the ammonia equilibrium over a wide range of temperatures and pressures have been carried out by

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[1] D R P 17070 1881

[2] Austr P 45,2938, 1895

[3] F P 313950 1901

[4] *Zeitsch anorg Chem*, 1905 **43** 111 *Ber* 1907, **40**, 2144 *Zeitsch Elektrochem*, **14**, 181, 513, 1908, 1910, 1913, also Eighth Int Congress App Chem, New York, 1912

Larson and Dodge[1] and by Larson.[2] From these data, and those of Haber at 30 atmospheres, empirical equations have been constructed to yield the value for the equilibrium constant, K_p, at any temperature and the four pressures, 30, 300, 600, and 1000 atmospheres. If the equation has the general form

$$\log K_p = \frac{a}{T} + b \log T + cT + dT^2 + C,$$

the coefficients and constants have the following values:

Pressure in Atmospheres.	a	b	c	d	C
30	2074·8	2·4943	$1{\cdot}256 \times 10^{-4}$	$1{\cdot}8564 \times 10^{-7}$	2·099
300	2074·8	2·4943	$1{\cdot}256 \times 10^{-4}$	$1{\cdot}8564 \times 10^{-7}$	2·206
600	2074·8	2·4943	$1{\cdot}0856 \times 10^{-4}$	$1{\cdot}8564 \times 10^{-7}$	3·059
1000	2074·8	2·4943	$2{\cdot}6833 \times 10^{-4}$	$1{\cdot}8564 \times 10^{-7}$	4·173

The percentages of ammonia, as calculated from these formulae, are given in the appended table for a variety of temperatures and pressures.

PRESSURE IN ATMOSPHERES

Per cent NH_3 in Equilibrium with a 1 : 3 $N_2 : H_2$ Mixture

Temperature	10	30	50	100	300	600	1000
325	10·38						
350	7·37	17·80	25·11				
375	5·25	13·35	19·44	30·95			
400	3·85	10·09	15·11	24·91			
425	2·80	7·59	11·71	20·23	35·5	53·6	69·4
450	2·04	5·80	9·17	16·36			
475	1·61	4·53	7·13	12·98	31·0	47·5	63·5
500	1·20	3·48	5·58	10·40	26·2	42·1	

Nernst and Jost,[3] by an application of the Nernst heat theorem to Haber's results, indicated that his figures were somewhat too high, and conducted a series of experiments at high pressures (viz. 70 atmospheres), when, as is indicated from the equilibrium equation, greater quantities of ammonia are formed. Haber repeated these experiments at 30 atmospheres, and it was finally shown that Nernst's figures were the more correct.

The Badische Co. operate two plants for ammonia synthesis. The original plant, at Oppau, was commenced in 1913, and was extended during the war years, so that by 1918 the plant had a capacity of

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[1] *J. Amer. Chem. Soc.*, 1923, **45**, 2918.

[2] *Ibid.*, 1924, **46**, 367.

[3] *Zeitsch. Elektrochem.*, 1907, **13**, 521; 1908, **14**, 373; 1910, **16**, 94.

200 tons per day The Leuna plant, at Merseburg, was erected in 1916 and had a capacity in 1921 of 400 tons of ammonia daily, to be raised to 800 tons per day when completed The combined output of the two works is adequate for the fixed nitrogen requirements of Germany when supplemented with other internal fixed nitrogen requirements, so that Germany may be regarded as independent of foreign supplies Partington[1] has given a condensed summary of the details of the Oppau plant, including the provisions for the manufacture and purification of the hydrogen-nitrogen mixture, data with respect to the synthesis bombs, recovery of the ammonia produced, power requirements, and personnel His outline may be taken as typical of the process as operated at Merseburg, and, probably, at the post-war factories of the General Chemical Company at Syracuse, N Y, and at Billingham, England, the factory of the Brunner-Mond Corporation Partington[2] cites the main differences between the Oppau and Merseburg factories in a subsequent article

The solution of the problem of a suitable catalyst for ammonia synthesis appears to have been found in the use of some form of an iron catalyst The activity of such a catalyst is greatly dependent on its method of preparation, together with the presence of certain promoters and the entire absence of certain catalyst poisons Whilst the patents of the Badische Co[3] indicate that promoters such as molybdenum, tungsten, cobalt, and uranium may be used in considerable proportions in an iron catalyst, technical practice seems to have made use of an iron catalyst containing only small amounts of promoter oxides, such as alkalis, alumina, and the like Extensive investigations of the properties of such iron catalysts under varying pressures, temperatures, gas velocities, and technical poisons have been reported by the research workers of the U S Fixed Nitrogen Research Laboratories[4] These researches have led them to the conclusion that the most active technical iron catalysts are to be produced from a fused iron oxide containing small amounts of *both* acidic and basic oxide promoters, such as 0 5 per cent alumina and 0 5 per cent potash

Claude process.—Claude has developed a process of ammonia synthesis from the elements of which the predominant difference from the Haber process as operated in Germany is the much higher pressure used by Claude For this change a most far-reaching and fundamental importance and distinction is claimed[5] The table, already given, of the variation of equilibrium concentration with pressure at various temperatures will show the advantage, as far as possible, ammonia yield per gas passage, which can be achieved by operating in the range of pressures suggested by Claude, 600-1000 atmospheres as opposed to the 200 atmospheres normally used in the Haber process. At 600° C. and at 900 atmospheres, the pressure used by Claude, a 30 per cent conversion can be theoretically attained as against a possible 9 per cent conversion at 200 atmospheres.

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[1] *J Soc Chem Ind* 1921, **40**, 99R

[2] *J Soc Chem Ind*, 1921, **40**, 144R

[3] B P 26167, 14/12/11 *ibid* 21151, 25/9/11.

[4] *Chem and Met Eng*, 1922, **26**, 493, 555, 588, 647, 683

[5] West, *J. Soc Chem Ind*, 1921, **40**, 420R

The advantages claimed for operation at super-pressures of the Claude type are several. The power costs for compression vary as the logarithm of the pressure, so that the power required for compression to 1000 atmospheres is only 50 per cent greater than that required for compression to 100 atmospheres. Owing to the small volumes occupied by the gases at these high pressures the apparatus as a whole is proportionately smaller and the tonnage of steel involved in unit production of ammonia correspondingly low. A greater ease in maintaining the reaction process autothermally can be anticipated, owing to the high conversion factor, the exothermicity of the synthesis process providing the necessary heat. The yield of ammonia per unit of catalyst, other things being equal, will also be higher in the Claude process, so that a smaller amount of catalyst and smaller catalyst units per unit production should obtain. The low conversion efficiency in the Haber process compels the adoption of a circulatory system in which the gases after being freed from ammonia are returned to the incoming gases In the Claude process the yield is sufficiently high, so that the bulk of the ammonia may be liquefied by cooling the gases and the residual ammonia with unchanged nitrogen and hydrogen may be then passed through a further catalyst unit where further conversion occurs. Thus, with a small number of catalyst tubes in series with each other a conversion efficiency approaching 90 per cent can be readily achieved without any circulatory plant. The adverse effect of diluent gases on the equilibrium attained at a given pressure can also be shown to become proportionately less as the operating pressure increases. It seems therefore that the possibility exists of employing successfully, when operating at super-pressures, a nitrogen-hydrogen mixture of a lower order of purity than is employed in the operation of the Haber process This forms an item of considerable importance in the economy of the process, since it is in purification that the high cost of the nitrogen-hydrogen mixture occurs. Claude proposes to use hydrogen from coke-oven gas which will contain not only 1-2 per cent carbon monoxide but also saturated hydrocarbons. In the first unit of the synthesis process, the carbon monoxide is hydrogenated to methane in presence of spent catalyst, the water and any ammonia formed being removed prior to the entry of the gases to the catalyst unit proper. West[1] has given diagrammatic arrangements and plant details for such a method of operation. Technical development is in progress in France It was started in England but has been discontinued. Technical development in U.S.A. has been undertaken by L'Azote, Inc, at Charleston, W. Va.

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[1] *Loc. cit.*

THE CATALYSTS EMPLOYED IN THE PREPARATION OF CYANAMIDE

In 1894 Moissan showed that calcium carbide when pure could not absorb nitrogen[1] up to 1200°, but in the next year Rothe and subsequently Frank and Caro noted that technical carbides containing the usual impurities showed that rapid absorption could be obtained below 1100°, and thus laid the foundation of a very large industry. It was at once evident that the presence of catalytic substances materially hastened the process of absorption and permitted the reaction to proceed at a lower temperature. This latter point is specially important, as the absorption of nitrogen by alkali and alkaline carbides proceeds by two reversible reactions

$$CaC_2 + N_2 \rightleftarrows CaCN_2 + C,$$

$$CaC_2 + N_2 \rightleftarrows Ca(CN)_2$$

The quantity of cyanide formed always increases as the temperature is elevated, but is practically negligible in amount for calcium carbide up to 1100°. Any effective lowering of the temperature employed will thus effect an economy in the utilisation of both heating energy and nitrogen, as well as a simplification of the technical operations.

It was not until 1906, however, that the utility of adding any specific catalytic material to hasten the absorption of nitrogen was suggested. Carlson[2] proposed the use of calcium fluoride, and Polzenius that of the chloride.

The subject was carefully investigated by Bredig and Frankel,[3] who determined the effect of the addition of 10 per cent of catalytic material on the quantity of nitrogen absorbed in two hours at various temperatures. At 800° the addition of 10 per cent of calcium chloride effected a 22 per cent absorption, whilst 10 per cent of lithium chloride effected 17 per cent absorption, the carbide alone only absorbing some 3 per cent. The chlorides of the other elements of the alkalis and alkaline earths were not so active, their efficiency falling off with the increase in their atomic weights.

From these and other investigations it appears that the chief function of the catalyst is to act as a fusible solvent for the calcium carbide. Not only does the absorption of nitrogen proceed more rapidly in the flux, but at the same time fresh surfaces of the unfused calcium carbide are expressed to the action of the nitrogen by the removal of the reaction products. According to Foerster and Jacoby the unchanged lime in the commercial carbide also exerts a catalytic activity by producing incipient softening at 1100°, thus offering an explanation of Moissan's results. Calcium chloride has a greater solvent action on the carbide than calcium fluoride, possibly on account of its lower melting point, and is thus a more effective catalyst, being generally employed in a quantity not exceeding 10 per cent by weight of the crushed carbide.

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[1] *Compt. rend.* 1894, 1918.

[2] *Chem. Zeit.* 1906, **30**, 1261.

[3] *Zeitsch. Elektrochem.*, 1907, **13**, 69, 605; 1908, **14**, 365.

The use of potassium carbonate (4 per cent) has been suggested by Pollaci,[1] whilst recently the use of the relatively cheap sodium chloride has been advocated as the most suitable catalyst for operation on a technical scale. But little is known about the solubilities of calcium carbide, cyanamide, and nitrogen in these various solvents, and no determinations appear to have been made on the velocities of the reaction in such solvents, subjects which might very well repay investigation.

CATALYSIS IN THE PREPARATION OF NITRIDES

The only technical production of nitrides from atmospheric nitrogen was accomplished by Serpek in the Savoy. Although certain difficulties militated against the economic success of his earlier plants, yet on account of the apparent possibilities of some such process, some allusion must be made to Serpek's work.

Serpek's process was based upon the following reactions, obtaining aluminium nitride by the simultaneous reduction and azotisation of the oxide :

$$2Al_2O_3 + 6C \rightleftarrows 4Al + 6CO.$$
$$4Al + 3C \rightleftarrows Al_4C_3.$$
$$4Al + 2N_2 \rightleftarrows 4AlN.$$

Caro's investigations have shown that the dissociation temperature of the nitride is higher than that of aluminium carbide, and consequently the nitride is actually formed through the intermediary of the metal.

The optimum temperature for nitrogen absorption was found to be between 1800 and 1900 , above 2000 dissociation of the nitride commences.

Serpek's later experiments indicate that the temperature for rapid azotisation could be considerably reduced by the addition of certain catalytic material. His earlier claims as to the efficacy of the addition of small quantities of hydrochloric acid or sulphur dioxide to the nitrogen could not be substantiated, but a small quantity of hydrogen appears to exert a considerable catalytic activity. More important is the addition of catalysts to the solid reacting phase, such as the addition of small quantities of copper, iron, or manganese to the alumina. Serpek obtained good results with natural French bauxite rich in iron. Tucker and Read[2] confirmed these observations of Serpek. Fränkel[3] conducted a series of experiments on the relative activities of various forms of carbon, and arrived at the conclusion that finely divided carbon, such as soot, was most effective, rapid absorption taking place between 1500 and 1600°

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[1] *Zeitsch. Elektrochem.*, 1908, **14**, 565.

[2] *Trans. Amer. Electrochem. Soc.*, 1912, **22**, 67.

[3] *Zeitsch. Elektrochem.*, 1913, **19**, 362.

It will be noted that if the series of reactions given above actually represent the various equilibria between the different phases, then the ratio

$$\frac{(CO)^6}{(N_2)^2} \text{ or } \frac{(CO)^3}{(N_2)}$$

should be constant This was actually shown to be the case by this investigator, who found that with increasing temperatures the equilibrium concentration of carbon monoxide rose, as is indicated in the following table Total pressure, 1 atmosphere

Temperature	$K \frac{(CO)^3}{(N_2)}$	Per cent CO Equilibrium (Mean Figures)
1500	500	33
1600	4,500	57
1700	16,900	75

It will be noted that for low-temperature operation the gas must be as free as possible from carbon monoxide, thus limiting the employment of generator gas as a source of nitrogen

The Badische Co, in a series of patents,[1] protect the use of catalytic agents rather than copper and iron, and more especially the oxides of those elements which form stable nitrides, on reduction and azotisation, such as chromium, uranium, vanadium, molybdenum, zirconium, titanium, and silicon

CATALYSIS IN CYANIDE FORMATION

In 1835 Dawes noted the formation of cyanides in the blast furnace, and the investigations of Bunsen and Playfair[2] showed that these cyanides were produced by the interaction of atmospheric nitrogen with potassium salts and carbon present in the furnace The formation of sodium cyanide occurs according to the following equation

$$Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO - 138,500 \text{ cals}$$

Very many attempts to make a technical application of this reaction have been made As early as 1843 Possoz and Boissière erected smal factories at Grenelle and at Newcastle. The process failed on account of the action of the materials on the containing vessels at the high temperatures employed.

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[1] D R P. 243839, 235300 *et seq*

[2] *Rep Brit. Assoc.*, 1845, 185

That the high temperature necessary for reaction was the fundamental disadvantage of the process was quickly realised, and we find numerous suggestions for overcoming this difficulty. On the one hand we find attempts to replace the sodium carbonate by barium carbonate, made first by Margueritte and De Sourdeval in 1862 and reinvestigated by both Munro and Readman of the Scottish Cyanide Company. A higher yield of cyanide at somewhat lower temperatures is undoubtedly obtained, but the process appears to be uneconomic from the industrial standpoint.

In 1839 Thompson directed attention to the catalytic effects of finely divided iron in the original reaction, and the catalytic effects of other metals, especially manganese and chromium, were noted by Margueritte and De Sourdeval in 1860 and by Swan and Kendall in 1845. In 1916 Bucher[1] reinvestigated the original claims of Thompson, and the fixation of nitrogen as cyanide by this method may be said to be industrially successful, although the great potentialities in the method have not yet been fully developed.

In the absence of a catalyst, temperatures of the order of 1400° C. are required. If any form of gas heating be employed the difficulties in maintaining retorts intact at this temperature are extremely great. Electrical heating is better, but uneconomic except in certain districts. The mixture when fused is highly plastic and runs over the metals employed with great ease. The two important modifications introduced by Bucher were the briquetting of the reaction mixture of sodium carbonate coke and metallic iron. In a stream of nitrogen or producer gas, nitrogen is readily absorbed at from 920°-950° C., yielding briquettes containing 20-30 per cent of sodium cyanide.

The cyanide may be directly converted into hydrocyanic acid or to ammonia by treatment with steam, according to the reaction

$$NaCN + 2H_2O \rightarrow HCOONa + NH_3,$$

or it may be leached out with liquid ammonia,[2] in which sodium cyanide alone is soluble.

A pure form of carbon is necessary[3] materials produced by the thermal disintegration and partial combustion of hydrocarbons or from carbon monoxide, according to the reaction

$$2CO = CO_2 + C,$$

being more effective than coke.

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[1] *J. Ind. Eng. Chem.*, 1917, **14**, 543 , *Met. and Chem. Eng*, 1916, **14**, 513

[2] Clancy, *Met. and Chem. Eng*, 1920, **22**, 856.

[3] Thompson, *Met. and Chem. Eng.*, 1922, **26**, 124.

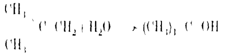
CHAPTER XI

HYDRATION, HYDROLYSIS, AND ALCOHOLYSIS

HYDRATION

SIMPLE hydration, or the direct addition of water by compounds, is a reaction which in certain cases may be promoted by catalytic agents. In the main, such reactions are confined to the fixation of water by unsaturated organic compounds with the production of oxygen-containing derivatives. Thus from unsaturated hydrocarbons, alcohols, aldehydes, and ketones may result. Similarly, careful hydration of certain nitriles will yield the corresponding amides, and, in a few cases, the hydration of imides has been noted. As a class, catalytic hydration processes have, hitherto, been unimportant technically, but recent developments in the synthetic production of alcohol from carbide as starting-point may give them a considerable importance in future application.

As with the processes of hydrolysis subsequently to be described, the mineral acids are active agents in promoting catalytic hydration. The transformation of isobutylene to trimethyl carbinol is accomplished in the cold in presence of sulphuric acid of moderate dilution.[1]



$$\begin{matrix} CH_3 \\ & C\,CH_2 + H_2O \rightarrow (CH_3)_3\,C\,OH \\ CH_3 \end{matrix}$$

Earlier still, the addition of water to pinene was shown to occur in presence of dilute nitric acid.[2]

$$C_{10}H_{16} + 3H_2O \rightarrow C_{10}H_{22}O_3$$

Similarly, hydrochloric acid accelerates the addition of water to crotonic aldehyde[3] according to the equation

$$CH_3\,CH\,CH\,CHO + H_2O \rightarrow CH_3\,CH\,OH\,CH_2\,CHO,$$

yielding the corresponding hydroxybutyric aldehyde. The processes of Wilson and Milly, previously cited in the discussion of hydrogenation of oils, also belong to this class of reaction, since, under the influence of sulphuric acid, iso-oleic acid, which is liquid is transformed by addition of water to solid oxystearic acid.[1] The reversibility of certain dehydration processes catalysed by acids, as, for example, the catalytic conversion of hydroxy-acids to lactones, also points to the catalytic activity of acids in simple hydration processes. The case of γ-butyrolactone formation from γ-hydroxybutyric acid studied by Henry[2] is an example in point, dilute acids being the catalytic agent :

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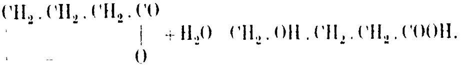
[1] Butlerow, *Annalen*, 1867, **144**, 22.

[2] Wiggers, *Annalen*, 1846, **57**, 247.

[3] Wurtz, *Bull. Soc. Chim.*, 1884 (ii), **42**, 286.



$$\begin{matrix} CH_2 . CH_2 . CH_2 . CO \\ \qquad\qquad\qquad | \\ \qquad\qquad\qquad O \end{matrix} + H_2O \quad CH_2 . OH . CH_2 . CH_2 . COOH.$$

The point has recently been specially tested by Johannson and Sibelius[3] with confirmatory results although a remarkable conclusion, however, is reached in that the hydration of β lactones is apparently not catalysed by hydrogen ions. Nor, as was demonstrated by Rivett and Sidgwick,[4] is the hydration of acetic anhydride catalytically accelerated by hydrogen ions.

Synthetic alcohol. In the development of processes for the synthetic production of alcohol, the possibility of utilising a process of hydration has been studied. The necessities of war and the great requirement of alcohol for the manufacture of munitions has stimulated investigation. In England, alcohol is mainly obtained by fermentation processes from grain. In Germany, production from potatoes by a combined hydrolytic and fermentation process has been largely used in addition to the grain fermentation process. The United States has developed a combined hydrolytic and fermentation process utilising sawdust as source of carbohydrate, whilst the Scandinavian countries and, more recently, Germany have devoted attention to alcohol recovery from the waste liquors in the sulphite-cellulose process. Nevertheless, the demand for alcohol is increasing so rapidly, more especially with a view to its use as a fuel for internal combustion engines that the synthetic production from cheap carbide is not without industrial possibilities. Indeed, it has been recently stated that successful production has now for some time been carried on by the Hoechst Farbwerken in Germany, and that a Swiss company, the Longa Electricity Works at Visp, Switzerland, covered during the war the alcohol requirements of their country with the synthetic product. The consumption of industrial spirit is increasing rapidly in England, and reached in 1916 1917 a total of upwards of four million gallons. It is obvious that the development of a synthetic process is of considerable importance in England also, as tending to economy in the utilisation of potential food supplies during periods of stringency.

Acetylene, obtained from calcium carbide by treatment of the latter with water, is the starting-point of the synthesis as developed in Germany and Switzerland. By a catalytic process of hydration, the acetylene is next converted into acetaldehyde according to the equation

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[1] Saytzeff, *J. pr. Chem.*, 1888 (ii), **37**, 284.

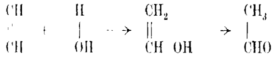
[2] *Zeitsch physikal. Chem.*, 1892, **10**, 98.

Ber., 1918, **51**, 480.

[4] *J. Chem Soc.*, 1910, **97**, 732.

$$CH\ CH + H_2O = CH_3\ CHO$$

The operation is presumably a two-stage reaction, the unsaturated alcohol first produced by simple addition of water changing by the ordinary shift of the labile hydrogen atom to an aldehyde, according to the scheme



$$\begin{array}{c}CH\\ \vdots\\ CH\end{array} + \begin{array}{c}H\\ |\\ OH\end{array} \longrightarrow \begin{array}{l}CH_2\\ \|\\ CH\ OH\end{array} \longrightarrow \begin{array}{l}CH_3\\ |\\ CHO\end{array}$$

The aldehyde thus obtained is available for hydrogenation to yield alcohol (p. 251), or, alternatively, may be oxidised to acetic acid (p. 209) for utilisation as such, or for subsequent conversion of acetic acid to acetone (Chapter XII.)

Various catalytic agents in different media have been suggested with the view of accelerating the hydration of the acetylene. Especially in most recent years has the patent literature of this process grown. In the main the various proposals suggest the conduct of the reaction by leading the gas into a warm liquid medium generally containing dissolved in it a suitable metallic salt to act as accelerator. Thus, according to the Griesheim Elektron Co.'s French patent No. 474246/1915 the acetylene is to be led into hot 20-25 per cent sulphuric acid, or 30-35 per cent phosphoric acid, or organic sulphonic acids, all in presence of the corresponding mercury salts. The British patent No. 5132/1915 suggests the passage of acetylene into glacial acetic acid at 80°-90° containing a dissolved mercury salt, the necessary water to be added as required. Meister, Lucius, and Bruning in U.S. patents 1151928 and 1151929/1915 suggest the addition of ferric salts, *e.g.* sulphate, to the acid solution of the mercury salt, together with a hexavalent chromium compound, *e.g.* chromic acid, in order to hinder the separation of mercury from the solution. D.R.P. No. 293070/1916, of the same firm, recommends as medium for the process metallic mercury in dilute acids. The Union Carbide Co., in U.S. patents Nos. 1213486 and 1213487/1917 claim the passage of acetylene into a solution of dilute sulphuric acid, a mercury salt, and the salt of a weak acid, *e.g.* a borate, or, alternatively, into a solution of the mercury salt and the acid salt of a strong acid, *e.g.* a bisulphate. The French patent, No. 479656/1916, of H. Dreyfus claims the passage of acetylene and water into solvents, (*a*) in which the mercury salt is soluble, *e.g.* acetic acid, or (*b*) in which acetylene is soluble, *e.g.* acetone. The aldehyde formed is to be converted direct into acetic acid by means of oxidising agents or by air in presence of catalysts such as cerium oxide, vanadium pentoxide, copper acetate, permanganates, manganese or copper nitrate, or platinum-palladium sponge. The oxidation to acetic acid is also claimed in the Badische Co.'s patent. D.R P. 294724, 1917, using atmospheric air in presence of iron salts and organic salts of alkalis and alkaline earths, including magnesium and aluminium. It is claimed that in this way the oxidation proceeds in the cold and no per-acids are formed. It is the formation of these latter which renders dangerous and uncertain the operations at present in use technically for the conversion of aldehyde to acetic acid, in which oxygen under pressure is used as oxidising agent in presence of such a catalyst as manganous acetate.

Ethylene as source of alcohol.--Ethylene was prepared pure from ethyl alcohol as early as 1795.[1] Its rehydration in presence of sulphuric acid was studied by Hennell[2] in Faraday's laboratory. It was re-announced by Berthelot[3] in 1855, and an attempt at large-scale production from the ethylene in illuminating gas was attempted in 1862. This proposal has been recently revived in England by Bury and Tidman, and operation has been attempted on a large scale at Skinningrove.[4] Absorption of the ethylene was there carried out with 95 per cent acid at 60°-80° C. To recover the alcohol, dilution of the acid is necessary. This constitutes one of the principal disadvantages of the process. If the acid is diluted to 64 per cent and distillation then undertaken, all the alcohol can be distilled, leaving a sulphuric acid of 80 per cent strength. The bulk of the alcohol obtained is in the form of a 15 per cent distillate.

With stronger sulphuric acid as absorption agent there is a decided increase in the production of diethyl sulphate from ethylene gas. The manufacture of this product, from ethylene in "cracked gas" for use as an ethylating agent, has been patented by Curme[5] and its uses have been detailed by Curme and Curme[6]

The velocity of absorption of ethylene in dilute sulphuric acid can be augmented by the addition of various substances to the acid.[7] Cuprous oxide, which is transformed by the acid into cuprous sulphate, is the most efficient among the substances used. In an earlier paper Lebeau and Damiens[8] had suggested addition of mercuric salts and also solutions of vanadium pentoxide or uranyl sulphate. Plant and Sidgwick[9] found that ethyl hydrogen sulphate has a distinct accelerating effect on the absorption process.

Isopropyl alcohol from propylene. The same reaction can be applied to propylene, an important constituent of cracked gas from petroleum distillation. Mann and Williams discovered[10] that a mixture of a mineral oil and sulphuric acid promotes the formation of esters, and this factor has proved of importance in the development of a practicable commercial process for the production of alcohols. Clough and Johns[1] have given details of the products of such commercial operation, the products in all cases being secondary alcohols, the range extending from isopropyl to secondary octyl alcohol.

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[1] *Crell's Ann.*, 1795, **2**, 196, 310, 430.

[2] *Phil Trans*, 1826, p. 240; 1828, p. 365.

[3] *Compt. rend*, 1855, **40**, 102.

[4] *J. Soc Chem Ind*, 1921, **40**, 86T.

[5] U.S.P. 1339947

[6] *Chem. Met. Eng*, 1921, **25**, 957.

[7] Damiens, *Compt. rend*, 1922, **175**, 585.

[8] *Compt. rend*, 1913, **156**, 557.

[9] *J. Soc. Chem. Ind.*, 1921, **40**, 14T.

[10] U.S.P. 1365043.

Higher homologues. Amylene with cold concentrated sulphuric acid and ice gives, on dilution, a solution from which dimethyl ethyl carbinol is obtained in 90 per cent yield. With hexene-1 and heptene-3,[2] the secondary alcohols are obtained with 85 per cent sulphuric acid. The use of 100 per cent acid promotes polymerisation.[3]

HYDROLYSIS

Processes of hydrolysis, that is to say, the process of resolution of a compound into two products with the simultaneous introduction into the resulting compounds of the component hydrogen and hydroxyl groups of water, have long been known to be sensitive to catalytic acceleration. Wilhelmy in 1850,[4] showed the catalytic influence of acids in the hydrolysis or "inversion" of cane-sugar, according to the equation

$$\underset{}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose}}{C_6H_{12}O_6} + \underset{\text{Laevulose}}{C_6H_{12}O_6}$$

by a study of the reaction velocity with which the process proceeded. This velocity could be determined with ease, as the progress of the reaction was accompanied by a change in the optical rotatory power of the system, not only in degree, but also in sign. Hence the term "inversion" of cane-sugar.

Similarly with esters, their hydrolysis to alcohol and acids may, in many cases, require years for completion if water alone is employed as the hydrolytic agent. On the contrary, in presence of small quantities of mineral acids, hydrolysis may be completed in a few hours, and all acids behave in like manner though in varying degree. This catalytic influence of acids is also found in the hydrolysis of other organic compounds, such as amides, acyl derivatives, imido esters, and ketonic acids. As, in general, such reactions proceed slowly, the rate of progress is susceptible of careful measurement, and consequently they have formed suitable material for the investigation of catalytic processes.

The inversion of cane-sugar, which may be taken as the type of all hydrolyses of various sugars and carbohydrates, has been investigated since the work of Wilhelmy already cited, by numerous observers. Wilhelmy showed, experimentally, that the velocity of inversion at any moment was proportional to the concentration of the sugar at that moment. This discovery was made prior to the formulation of the law of mass action, and is an experimental consequence thereof, provided that the water is present in large excess and changes only negligibly in concentration during the reaction. The mathematical expression of this unimolecular process is given by the equation

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[1] *J. Ind. Eng. Chem.*, 1923, **15**, 1030.

[2] Adams, Kamm and Marvel, *J. Amer. Chem. Soc.*, 1918, **40**, 1950.

[3] Brooks and Humphrey, *J. Amer. Chem. Soc.*, 1918, **40**, 822.

[4] *Pogg. Ann.*, 1850, **81**, 413, 499.

$$\frac{dx}{dt} = K(a - x),$$

where K is a composite constant, including the reaction constant k and the concentrations of water and catalyst which are sensibly constant throughout the process; a is the original concentration of sugar and x the amount converted in time t. On integration the equation becomes

$$K = \frac{1}{t} ln \frac{a}{a - x},$$

from which, with the aid of the experimental determinations, reaction velocity constants may be calculated. The progress of the change in sugar inversion as well as in ester hydrolysis is readily followed, by polarimetric determinations in the former and by determination of the increase of acidity of the solution in the latter case.

The catalytic activity of acids upon the two reactions was studied by varying the concentration and nature of the acid employed. The researches of Lowenthal and Lennsen (1862) of Fleury (1876), of Ostwald (1884), and of Spohr (1885-1888) gave Arrhenius (1889) abundant material upon which to base his deductions concerning the part which acids played in the catalytic process. It was readily shown that increase in concentration of the acid gave increased velocity of inversion, the increase being roughly, though not exactly, proportional to the increase in concentration. It was further demonstrated that in equal concentrations, different acids varied greatly in their catalytic activity.[1] This was greatest with the strong mineral acids investigated. Thus, a 0·5 normal solution of hydrochloric acid catalysed the inversion 250 times more rapidly than acetic acid of the same normality. Closely parallel results were obtained in a study of the corresponding hydrolysis of esters using such acids.

It is common knowledge how this behaviour of acids towards sugar inversion and ester hydrolysis was coupled, by Arrhenius, with his observations upon the electrical conductivity of aqueous solutions of acids, and how, as a result, the theory was developed that the catalytic activity of acids was due to the hydrogen ions which acids yielded when in solution. The strong mineral acids, according to the theory, possessed a high catalytic activity, because, in solution, their dissociation into ions was practically complete. Conversely, with weak acids, feebly dissociated, the catalytic activity was small.

The effect of the addition of a neutral salt of a weak acid upon the catalytic activity of the acid assisted considerably in the development of the dissociation theory. Arrhenius was able to show that the addition, for example, of sodium acetate to a solution of acetic acid enormously depressed the catalytic activity of the acid. Thus, a 0.25 normal solution of the salt, when added to a solution of the acid of the same normality, reduced its activity in the ratio of 0.74 : 0.0105. Assuming that the addition of sodium acetate repressed the degree of dissociation of acetic acid and therefore the hydrogen-ion concentration in accordance with the law of mass action, the calculated variation in the reaction velocity should be in the ratio 0.74 : 0.0100, a remarkably close agreement with the experimentally determined figures. Accumulating evidence of such nature led rapidly to the acceptance, not only of the hydrogen-ion theory of acid catalysis, but also to acceptance of the dissociation theory itself.

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[1] Ostwald, *J. pr. Chem.*, 1883, 27, 1.

With strong acids the quantitative factors were by no means so readily explicable. Exact proportionality between the hydrogen-ion concentration, as calculated from electrical conductivity, and the catalytic activity does not obtain in solutions of strong mineral acids, except, as was demonstrated by Palmaer,[1] in extremely dilute solutions. The increase in activity is always somewhat greater than the increase in hydrogen-ion concentration as determined by electrical conductivity measurements. Moreover, the influence of neutral salts of strong acids is very remarkable. It is found, for example, that in ester catalysis the addition of a normal solution of potassium chloride accelerates the catalytic activity of a 0.1 normal solution of hydrochloric acid by as much as 22 per cent, whereas, on the simple dissociation theory, as with acetic acid, a diminution of reaction velocity would be expected. This interesting abnormality, the so-called neutral salt action, has occupied the attention of a considerable number of investigators down to the present day, and so far no completely satisfactory explanation of the phenomena is forthcoming.

It has been frequently shown, and especially by Poma[2] in an extended series of measurements, that, in ester catalysis, the influence of neutral salts on the velocity of reaction depends in high degree on the nature of the anions, and that the influence of the cations is either non-existent or within the limits of experimental error. Thus, the chlorides of potassium, sodium, lithium, barium, strontium, and magnesium cause the catalytic power of the hydrochloric acid to be enhanced to approximately the same degree in equal concentrations of salt. Further, the influence of salts differs in degree with the anion employed. In descending order of accelerating effect come the chlorides, bromides, nitrates, and iodides, when used with the corresponding acid. This observation may be extended to all acids by stating that the accelerating action diminishes with diminishing degree of dissociation as calculated by conductivity methods and finally becomes, with weak acids, not an acceleration but a retardation, as previously mentioned in the case of acetic acid.

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[1] *Zeitsch. physikal. Chem.*, 1894, **22**, 492.

[2] *Gazzetta*, 1911, **41**, 353.

Early suggestions of Arrhenius to account for neutral salt action are twofold. It was assumed[1] that there exists in solution an equilibrium between the active and inactive forms of the substrate, and that this equilibrium was displaced by increase of ionic concentration in the direction of increase of active modification, thereby resulting in increase of reaction velocity. An attempt at precise differentiation between active and inactive molecules in chemical change has recently been made in the previously discussed papers by Lewis,[2] in which papers the concepts of critical energy and critical increment of energy necessary to produce reaction are introduced. The active molecules are assumed to differ from the inactive in respect of their internal energy, which is considerably greater than that possessed by an average molecule of the substance at the temperature in question. The fact that the critical energy is high indicates that only a very small fraction of the total molecules will be active at any moment. In the second place, Arrhenius suggested that the ions of the neutral salt have some action on the hydrogen ions of the acid and thereby contribute to increased activity.[3] For strong acids alone, this could be formulated by an equation of the form

$$K = a(H^{\cdot}) + b(H^{\cdot})_2,$$

where K is the velocity constant. Lunden[4] extended this idea to the mathematical interpretation of the experimental results in presence of neutral salts.

A considerable body of opinion has sought the explanation of the accelerating influence of neutral salts by attributing to the latter a concentrating effect on the acid catalyst, due to withdrawal of solvent water from the solution. The solvate theory of H. C. Jones in America is capable of such application. In England, an investigation of the processes operative in solution by H. E. Armstrong and his co-workers has been animated with a similar view-point. In particular, the studies of Caldwell,[5] Whymper,[6] Armstrong and Watson,[7] Worley[8] may be mentioned in this connection. The view is put forward that hydrolysis is an associative process involving the interaction of associated complexes, the hydrated hydrolyte and hydrated catalyst. By studies of the inversion of sucrose and of the hydrolysis of esters, the apparent molecular hydration values of acids and neutral salts have been determined, and the accelerating influences observed in the study of reaction velocity are attributed to such agencies. The theory as developed is directly opposed to the generally accepted electrolytic dissociation theory, and it is claimed[1] that the facts disclosed go far to show that this hypothesis is no longer tenable. The associative theory has earned, however, considerable criticism. Thus, Senter[2] directs attention to the fact that the relative neutral salt action of different salts is not that of their ordinary degree of hydration. Further, the relatively slight influence of temperature on neutral salt action[3] is, according to Senter, in marked contradistinction to the general effect of temperature on hydration.

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[1] *Zeitsch. physikal. Chem.*, 1889, **4**, 226.

[2] *J. Chem. Soc.*, "Studies in Catalysis", parts i.-ix. (1914–1918).

[3] *Zeitsch. physikal. Chem.*, 1899, **28**, 329.

[4] *Ibid.*, 1904, **49**, 189.

[5] *Proc. Roy. Soc.*, 1906 (*A*), **78**, 272.

[6] *Ibid.*, 1907 (*A*), **79**, 576.

[7] *Ibid.*, 1907 (*A*), **79**, 579.

[8] *Ibid.*, 1912 (*A*), **87**, 604.

An accumulation of evidence during recent years has given support to the theory that, in homogeneous liquid systems, the undissociated molecule of a catalytic substance, in addition to the ions, possesses a certain definite catalytic activity, which, in a given reaction, bears a definite relation to that of the ion which is catalytically active. Researches of Senter,[4] of Acree and Nirdlinger,[5] and of Lapworth[6] directed attention to the general principle involved, while, in the last-named research, the special application to hydrogen chloride was pointed out in connection with the work on the effect of water on the activity of acids in alcoholic solution. Researches of Goldschmidt on catalytic esterification by acids in alcoholic solution (p. 369), of Acree and his co-workers[7] on numerous reactions both catalytic and non-catalytic, of Bredig, Millar, Braune, and Snethlage on the catalytic hydrolysis of diazoacetic esters (p. 319), have, more recently, yielded contributory evidence to the view-point that undissociated molecules might possess a specific catalytic activity. Reviewing the available data, Snethlage was led to suggest,[8] in reactions catalysed by acids, and therefore in ester hydrolysis and the inversion of cane-sugar, that the greater the strength of the catalysing acid, the greater is the catalytic activity of the un-ionised portions as compared with the activity of the ion. If one assumes that the reaction velocity is composed of two velocities determined by the catalytic activity of molecule and of ion acting in proportion to their concentration, the velocity may be expressed by the equation

$$R = n_H K_H + n_m K_m,$$

where n refers to the concentration, K to the catalytic activity of ion or molecule, H or m.

The evidence to be brought forward in the succeeding chapter on the kinetics of esterification and other dehydration processes occurring both in alcohol and in water solutions indicates an alternative to a theory of the catalytic activity of the undissociated molecule. The researches of Lapworth and his co-workers (pp. 369, 370) indicate that the active catalytic agent may be the non-hydrated hydrogen ion. The abnormal variations of acid catalytic activity with change in acid concentration, addition of neutral salts or solvents, would in such case be ascribed to the influence of these several factors on the equilibria

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[1] See especially Worley, *Phil. Mag.* (1911).

[2] *J. Chem. Soc.*, 1907, **91**, 462.

[3] See Taylor, *J. Amer. Chem. Soc.*, 1915, **37**, 551.

[4] *J. Chem. Soc.*, 1907, **91**, 460.

[5] *Amer. Chem. J.*, 1907, **38**, 489.

[6] *J. Chem. Soc.*, 1908, **93**, 2197.

[7] *Amer. Chem. J.*, 1912, **48**, 352.

[8] *Zeitsch. Elektrochem.*, 1912, **18**, 539; *Zeitsch. physikal. Chem.*, 1913, **85**, 211. See also Taylor, *Zeitsch. Elektrochem.*, 1914, **20**, 202.

$$H^{\cdot} + nH_2O \rightleftarrows H^{\cdot}nH_2O,$$

where n may be a very variable quantity determined not only by the water concentration but also by the concentrations of the other constituents of the solutions. A beginning only has been made in the quantitative development of this idea.[1] The most important experimental contributions to the theory are to be found among dehydration processes (Chapter XII., *q.v.*). What is concluded for such reactions, as to the nature of the catalytic agent, will apply also, with equal force, to the reverse processes of hydration and hydrolysis.

The solution of the problem of reaction velocity in its relation to catalyst concentration has been sought also, as pointed out in the chapter on the kinetics of homogeneous catalytic reactions, in terms of the activities of the catalyst species. Thus, for example, in the investigations of Harned,[2] Åkerlof,[3] Lewis and his co-workers,[4] Bronsted and his students,[5] the attempt has been made to correlate the reaction velocities obtained with the data as to activity of the catalyst, deduced from studies of the electromotive behaviour of acid-salt systems, freezing point, distribution experiments, and the like. This attempt is actually parallel to that discussed in the preceding paragraph. The one attempts a thermodynamic formulation of the catalyst concentration; the other attempts a kinetic picture of the catalytic process. A more extended treatment of Brönsted's point of view will be given in succeeding paragraphs of this chapter when dealing with the larger and more variable salt effects obtained in other hydrolytic processes. It is only necessary here to point out that in the inversion of sugar and the hydrolysis of esters in presence of strong acids the salt action is, actually, small compared with that occurring in other processes, such, for example, as the decomposition of persulphates in presence of iodide ions, the hydrolysis of dibromsuccinic acid, and the like. For whereas in these latter cases the ratio of reaction velocities in 0·1 and 0·2 normal total ion concentrations amounts to $k0{\cdot}1/k0{\cdot}02 = 1{\cdot}8\text{-}2{\cdot}0$, the corresponding ratio for 0·1 normal salt solutions with acid amounts in cane-sugar inversion to about 1·03-1·04, and in ester hydrolysis to about 1·02.

The catalytic activity of the acid in such reactions as ester hydrolysis is now fairly generally attributed to the formation of intermediate

[1] Rice, *J. Amer. Chem. Soc.*, 1923, **45**, 2808.

[2] *J. Amer. Chem. Soc.*, 1918, **40**, 1462; 1922, **44**, 2104.

[3] *Zeitsch. physikal. Chem.*, 1921, **98**, 260.

[4] *J. Chem. Soc.*, 1920, **117**, 1120; 1922, **121**, 1613.

[5] *Zeitsch. physikal. Chem.*, 1922, **102**, 169.

additive compounds. The systematic investigation of the formation of such compounds has recently been undertaken by Kendall and his co-workers,[1] and the results obtained are not without significance in the interpretation of strong acid catalysis and neutral salt action. By the examination of a number of ester-acid systems, using a freezing-point method, it was shown that the formation of oxonium compounds between ester and acid followed the same general principles obtained in earlier work on compound formation in other organic systems. For example, combination is most marked between strong acids and esters of weak acids. Further, the extent of compound formation decreases with decrease of acid strength, although, even with the weakest acid, compound formation was indicated by the form of the curves, without, however, any isolation of the compound. By making the radicals R and R_1 of the ester $R.COOR_1$ more negative, the degree of compound formation also diminished. The concordance of these results with the facts of catalytic activity previously put forward is sufficiently obvious to prompt the conclusion that the hypothesis of the intermediate additive compound is fundamentally sound. It is made the more conclusive by the studies of Stieglitz and his co-workers on the parallel case of the hydrolysis of imido-esters (p. 339).

The dependence of the velocity of hydrolysis of esters in presence of catalysing acids on the nature of the ester substrate was extensively investigated by Lowenherz,[2] who showed that the influence of the alcohol radical of the ester was comparatively slight, but that the velocity was to a marked degree dependent on the nature of the ester acid. Thus, ethyl formate hydrolyses twenty times more rapidly than ethyl acetate; the velocities with methyl, ethyl and propyl acetates are all approximately equal to one another, whereas with the homologous series of esters of acetic, propionic, butyric, and valeric acids the velocity of hydrolysis becomes increasingly slower with increasing complexity of acid, that of the formate being one hundred times greater than the velocity of hydrolysis of the valerate. With aromatic esters the velocity is even slower. Ethyl acetate hydrolyses one hundred and fifty times more rapidly than ethyl benzoate with the same concentration of catalysing acid.

Alkaline hydrolysis of esters. The resolution of an ester into hydrolytic products may also be accelerated by the use of alkalis. In this case the acid produced by hydrolysis is immediately neutralised by the alkali present, giving the corresponding alkali salt of the acid. The net result of the process may be represented by the general equation

$$R.COOR_1 + M.OH = R.COOM + R_1OH$$

Thus, in the course of the reaction, both ester and alkali disappear, the reaction proceeding until one or other constituent is completely used. Obviously, also, the reaction is bimolecular, and the reaction velocity equation is of the form

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[1] See *J. Amer. Chem. Soc.*, 1916, **38**, 1712; 1917, **39**, 2323.

[2] *Zeitsch. physikal. Chem.*, 1894, **15**, 389.

$$\frac{dx}{dt} = k(a-x)(b-x),$$

where a and b are the concentrations of ester and alkali, and x the amount of each transformed at time t. Expressed in the integrated form, this equation gives

$$k = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)},$$

with which the reaction constant k can be calculated from the measurements of the concentrations of the reacting substances. As, in the process of reaction, the alkali is converted to a neutral salt, the velocity with which the action proceeds can be determined by titration with standard acid.

In this manner Reicher was able to study [1] the velocity of hydrolysis or saponification, as it is better expressed when speaking of alkaline hydrolysis, of esters in presence of sodium, potassium, and calcium hydroxides. It was demonstrated that, in dilute solutions of alkali, the velocity of saponification was independent of the nature of the base, proportional, however, to the alkalinity of the solution. These results led later to the conclusion that the hydroxyl ion was the active hydrolytic agent; that, moreover, the reaction was truly catalytic in nature, the catalyst, however, being removed from the system by the subsequent and independent interaction of the base with the acid formed by hydrolysis.

The relation of velocity of saponification to constitution of ester has, from Reicher's experiments onward, attracted considerable attention. The influence of the alcohol is apparently more marked than in the case of hydrolysis by acids, isobutyl acetate being hydrolysed only one-half as rapidly as methyl acetate in the same strength of alkali.[2] The influence of the nature of the acid radical is by no means so pronounced, however, since, with dilute soda at 14, the velocity of saponification of the acetate is approximately double that of the isobutyrate, six times that of the isovalerate, and four times that of the benzoate. Later work [3] on the constitutional influence of the acyl grouping shows, however, that the velocity is determined largely by the complexity of the acyl group and more especially by substituents in close proximity to the carbonyl group. Assuming that hydrolysis is preceded by formation of an intermediate additive compound or ion complex, it may be deduced by analogy with the results of Kendall on acid hydrolysis, previously cited, that the strength of the acid forming the radical in the ester would also determine the velocity of the hydrolysis. Experimental test shows this to be the case.

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[1] *Annalen*, 1885, **228**, 257.

[2] Arrhenius, *Zeitsch. physikal Chem.*, 1887, **1**, 110.

[3] Hjelt, *Ber.*, 1896, **29**, 1864; Kellas, *Zeitsch. physikal. Chem.*, 1897, **24**, 243; Sudborough and Feilman, *Proc. Chem. Soc.*, 1897, **13**, 243, Findlay and Turner, *J. Chem. Soc.*, 1905, **87**, 747; Gyr, *Ber.*, 1908, **41**, 4308, Findlay and Hickmans, *J. Chem. Soc.*, 1909, **95**, 1004.

The addition of neutral salts to systems of alkaline hydrolysis of esters may either repress or accelerate the velocity of saponification, as was shown by Arrhenius[1] and by Spohr.[2] The phenomenon of neutral salt action in alkaline hydrolyses is, however, much more obscure and unformulated than is the case with acid hydrolysis, the same regularities being by no means observable. Thus, in the hydrolysis of sodium chloroacetate by sodium hydroxide Senter showed[3] that the addition of salts accelerated the reaction. Bronsted's treatment of such cases will be given at a later stage (p. 346).

TECHNICAL APPLICATIONS OF HYDROLYSIS

The hydrolysis of sugars and of polysaccharides, as well as of esters, finds extended technical application in several large industries. The whole soap industry is concerned with the hydrolysis of the fatty acid esters of glycerine, and, in the tallow industry, fatty acids are obtained by hydrolysis of the corresponding glycerides. The manufacture of glucose from starch is an example of the hydrolysis of polysaccharides and production of invert-sugar, whilst the degradation of cellulose by hydrolysis to fermentable sugars capable of yielding alcohol for industrial purposes is an industry of recent growth and of considerable promise for subsequent development. The more important scientific aspects of these technical applications merit individual discussion.

The manufacture of glucose. The industrial development of catalytic hydrolysis of polysaccharides for the production of glucose has attained considerable proportions. As raw material for the preparation, starch or starch-containing materials are employed. In England, rice rice starch, maize, and sago are chiefly used. Potato starch finds application in Germany. In America, the starch from maize or Indian corn is the principal material. All such materials yield, with acids, products containing more or less of the glucose desired. The reaction occurring may be represented by the general equation

$$(C_6H_{10}O_5)x + xH_2O = xC_6H_{12}O_6$$

As hydrolytic agents, dilute acids are employed, the acid functioning as catalyst. Various acids find technical application. In Europe, sulphuric acid is the usual reagent used. In America, hydrochloric acid is mainly employed. Other strong acids, such as nitric and phosphoric acids, may be employed if local circumstances are favourable to their use. Even sulphurous acid has been suggested as a hydrolytic agent.

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[1] *Zeitsch. physikal. Chem.*, 1887, **1**, 110.

[2] *Ibid.*, 1888, **2**, 1194.

[3] *J. Chem. Soc.*, 1907, **91**, 462.

Heat is always employed to assist the process of hydrolysis. Closed converters of cast-iron, copper, or gun-metal have replaced, almost entirely, the original lead-lined open converters made of wood. With the closed type of converter the temperature is maintained by injection of steam up to pressures of 30 lbs.

With sulphuric acid a 5 per cent aqueous solution is employed in the open system. When pressure is simultaneously used, the percentage of acid may be reduced to as low as 0·5 per cent For unit weight of dried starch, approximately two and a half units by weight of the acid solution are required. In modern American practice it is customary to employ large volumes of water with which a paste of the starch is made, and to which small quantities of pure hydrochloric acid are added to assist the hydrolytic process. The whole mass is subjected to a high temperature, under pressure, in massive copper converters.

Hydrolysis occurs in definite stages. After a short period of heating, the starch is completely converted to dextrins and maltose. At this stage, it no longer gives the blue coloration with iodine, but a reddish-brown coloration indicating the presence of α-dextrin. With further action of the acid, the dextrins and maltose yield glucose. The absence of the dextrin is determined by the non-appearance of a precipitate on addition of twice the volume of alcohol to a sample of the liquor. Care must be taken to avoid carrying hydrolysis too far, as glucose may itself be attacked by the acid liquor. The process of hydrolysis may be stopped at any desired stage according to the product desired. If the syrup is required, the process is stopped immediately iodine gives a port wine colour to the solution. Consequently, corn syrup contains marked quantities of dextrin, averaging 40 per cent, with an equal quantity of glucose and 20 per cent of water. Solid glucose is obtained from solutions which no longer yield the dextrin test, and the anhydrous sugar therefore generally contains less than 1 per cent of this impurity, with not more than 5 per cent of water.

Naturally, the time required for completion of the hydrolytic process is governed by the three factors: mean temperature during the operation, the pressures employed, and the concentration of the catalytic agent. The nature of the final product also governs the length of the process. For the solid product, the average time required is about 1½ hours; for the syrup, half this period or less.

After hydrolysis, the catalytic agent is removed by neutralisation with alkalis. For sulphuric acid, a milk of finely ground chalk in water is employed, the precipitated sulphate is allowed to settle, and the clear liquor drawn off. Soda ash is used in American practice, the mixture being left just faintly acid. Excess of alkali is avoided, as, even in small traces, it imparts coloration to the liquid in the subsequent operations. The filtered liquor is then partially concentrated and passed through filters of decolorising charcoal, the resulting clear liquor being then concentrated in vacuum pans until the desired concentration is reached On cooling, the mass crystallises

Glucose from cellulose.—Wood cellulose may form a considerable source of glucose supplies in the future, and efforts to achieve the hydrolytic conversion on a technical scale have been numerous The fuel problem for the motor industry has stimulated interest in the process, since the fermentable sugars produced can readily be employed in the manufacture of alcohol The disintegration of cellulose is, however, a matter of great difficulty, and, as yet, it has not been so far generally developed as to compete commercially with the processes employing starch

The various aspects of the problem have been presented somewhat as follows by F W. Kressman of the U S Forest Products Laboratory, Madison, Wisconsin, and in a paper by the U S Department of Commerce, "By-products in the Lumber Industry" There is a large margin in the cost of raw material in favour of alcohol from wood waste as against alcohol from grain The fuel charges of a wood-waste installation are always a much smaller item than in the case of a grain distillery, since most sawmills produce waste considerably in excess of their own power requirements From wood waste, however, a yield of 20 gallons of proof spirit per ton of wood represents good practice as compared with 80 gallons per ton from corn It is obvious, therefore, that the amount of material handled in certain parts of a plant producing alcohol from wood will be four times as great as in a grain distillery of equal capacity Hence the capital outlay and costs of operation will be somewhat greater Portions of the plant, however, and among these the larger items, as, for example the fermenter and the still equipment, will not need to be larger so that one of the major costs of production will not be increased The balance of points, it will be observed, is distinctly even, and with favourable conditions the alcohol industry from wood cellulose may leap forward as a commercial success Hitherto, this has not been realised except in particular cases

The processes employed for the production of alcohol from wood may be classified in two groups, (a) hydrolysis of cellulose to fermentable sugars by means of dilute mineral acids acting as catalysts, (b) processes in which the wood is dissolved in concentrated acid, hydrolysis being effected on subsequent dilution This latter classification has not yet received commercial application owing to the high cost of the acid and the expense and labour of recovery of the spent acid liquor The French patent of Ekstrom[1] is of this type Treatment with 95 per cent sulphuric acid for twenty minutes, followed by dilution to 1 per cent acid strength and digestion for a period of one to five hours, was specified for high conversion of cellulose to fermentable sugars

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[1] F P 380358, 1907

In the dilute acid processes, Simonson[1] employed dilute sulphuric acid of 0·5 per cent strength. A pressure of 9 atmospheres was employed, the material being in the proportions of one part of wood to four parts of the dilute acids. Digestion for a period of one-quarter of an hour was said to yield fermentable sugars sufficient to give a yield of alcohol equal to 6 per cent of the dry wood employed.

In some recent modifications of the dilute acid process the operations have been directed towards the use of hydrochloric and sulphurous acids with a considerably smaller moisture content. The work of A. C. Classen directed attention more particularly to the use of sulphur dioxide as the hydrolytic agent, and its commercial development is being actively pursued. An acid concentration of 1 per cent is employed. The moisture content is kept as low as possible for the sake of economy in the subsequent neutralisation and concentration processes, as well as for greater ease of regulation of the temperature time factors, which are of great importance for successful operations. It has been found that a 50 : 50 wood-acid liquor ratio is not above the saturation limit of the wood, which can therefore be handled in conveyers as with the original sawdust. The heating is effected by means of steam, the operating pressures being from 75-100 lbs.

The separation of the sugars from the woody residue of the hydrolytic process is effected in standard beet-sugar diffusion batteries provided with suitable acid-proof linings. Neutralisation of the acid liquors is generally effected by means of lime, milk of lime, or a high-grade limestone. The fermentation of the sugars is carried out in accordance with standard practice with a four-day fermentation period. The distillation and rectification of the alcohol are standard practice and involve no special problems. (Fig. 17.)

As to yields, obtained and possible, it may be observed that from 25-28 per cent of the anhydrous wood may be rendered soluble, of which as much as 80 per cent is fermentable sugar. Thus, a yield of 20-22 per cent of saccharoses, corresponding with 10-11 per cent of ethyl alcohol, equivalent to 35 gallons of 95 per cent alcohol per dry ton of wood, represents the maximum goal. Actually, the average practical yields scarcely exceed half this amount, a figure of 20 gallons per dry ton being now good practice. Evidently there is a considerable margin for improvement.

The residue after the sugars are removed amounts to 70 per cent of the original wood, and this also possesses a definite fuel value which may be utilised in the plant.

Thus far the large-scale technical operations of the process have been confined to the United States, where, within the last ten years, according to a recent statement by Tomlinson,[2] two plants have been

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[1] *Zeitsch. angew. Chem.*, 1898, 195, 219, 962, 1007.

[2] Convention of Canadian Chemists, Ottawa, 1918.

in continuous operation, producing a high-grade alcohol at costs comparing well with those of other sources It may be expected that similar developments will occur in Canada and other timber-producing areas

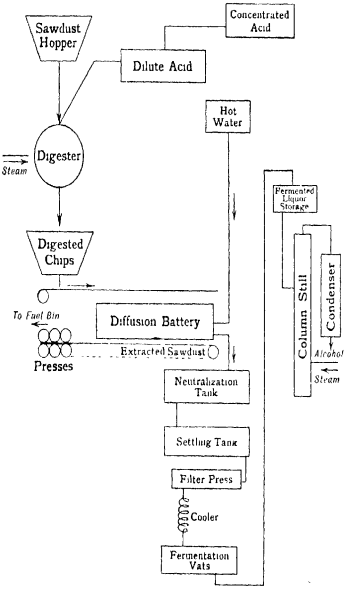


FIG. 17.

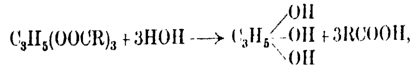
Sugars and alcohol in the sulphite paper pulp process.—The waste liquor from the production of paper pulp by the sulphite process contains fermentable sugars which may also be used as a source of alcohol. This process of alcohol production developed during the Great War to considerable proportions in Sweden and Germany, and may be expected to thrive whenever economic conditions are again favourable.

A comprehensive discussion of the sulphite liquor alcohol problem has been given by Haegglund and Bryant.[1] In the production of sulphite pulp, calcium bisulphite solution is used. Effort is made to use a cooking liquor with a high content of free sulphur dioxide. The solution normally employed will approximate to 2·5-3 per cent free and 1·1-1·2 combined sulphur dioxide. In cooking, 3·5-4 times as much liquor, by weight, as bone dry wood is used. The time of cooking is dependent on the strength of the liquor, the nature of the wood, and the working temperature. The direct cooking process, operating at 140°-145° C., occupies 10-12 minutes. The indirect process of cooking should not go to temperatures above 135° C. and takes from 15 to 20 hours.

With a constant combined sulphur dioxide content of 1·15 per cent Haegglund showed that the higher the concentration of free sulphur dioxide the quicker the sugar goes into solution. The maximum sugar formation was reached with a 3 per cent free sulphur dioxide in 15 hours at an operating temperature so controlled that, after 4-5 hours, the digester was 105° C. and attained a maximum temperature of 135° C. The higher the content of free sulphur dioxide the more readily were the sugars decomposed.

Haegglund states that neutralisation of the acid liquors was best carried out by a combination of fresh slaked lime for the preliminary neutralisation, during which the liquor is vigorously aerated, with or without oxidising catalysts, with a subsequent final neutralisation with pulverised limestone. The liquor, after neutralisation, is settled, cooled, and run into fermentation vats. A high resistant yeast is needed for the fermentation process. The yeast type XII. and the yeast mixture M of the Institute of Fermentation Industry in Berlin were specially recommended for this operation. Under favourable conditions the fermented liquor contains 1 per cent by volume of alcohol.

The hydrolysis or saponification of oils and fats. The principles of catalytic hydrolysis find extended industrial application in the hydrolysis of the glycerides in fats and oils for use in the soap, candle, and glycerine industries. The chemical reaction occurring in such hydrolysis may be generalised by the equation



$$C_3H_5(OOCR)_3 + 3HOH \longrightarrow C_3H_5\begin{cases}OH\\OH\\OH\end{cases} + 3RCOOH,$$

where R denotes any fatty acid radical. The reaction is a true case of a hydrolytic splitting of an ester into an alcohol and an acid, and, as in the cases previously treated, may be effected by water alone, but may be accelerated by the use of catalytic agents either acid or alkaline. When alkalis are employed to effect hydrolysis, conversion of the alkali and fatty acid to the corresponding salt occurs. This is, therefore, a true case of saponification. Actually in the industry the term saponification is applied to all the methods of promoting hydrolysis, both by acid and alkali, the term hydrolysis being confined to reports scientific in character. Whether by acid or alkali, the initial process is that generalised in the above equation, being followed in the case of alkalis by neutralisation of the free fatty acid with the formation of a soap.

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[1] *Paper*, 1917, **21**, No. 16 *et seq.*; also *Can. Dept. of Forestry*, Bull. No. 66, 1919.

The mechanism of the hydrolytic process may best be understood by reference to the hydrolysis of the glycerides of the simpler aliphatic acids, where, owing to the fair solubility of the glycerides in the catalytic medium, the conditions of operations are simpler and more readily controlled than is the case with the glycerides of the more complex fatty acids, which are but sparingly soluble, yield emulsions, and insoluble, or only partly soluble, acids. Such study shows that the hydrolysis of the glycerides occurs in successive stages, di- and monoglycerides being first formed as intermediate compounds yielding, finally, glycerine and the fatty acid. Thus Geitel[1] showed that the hydrolysis of triacetin, the glyceride of acetic acid, was apparently a unimolecular reaction, but that the velocities of hydrolysis of mono-, di-, and triacetates in dilute acids were in the ratios of 1 : 2 : 3. The parallel result with the acetates of glycol was demonstrated by Julius Meyer in 1907,[2] where the rates of hydrolysis of the two acetates were in the ratio of 1 : 2. Abel[3] and Kremann,[4] studying both acid and alkaline hydrolysis of esters of polyhydric alcohols, showed the same results as those of Geitel, and demonstrated that the apparent unimolecular nature of the hydrolysis of the complete glyceride was a mathematical consequence of the fact that hydrolysis occurred in the three successive stages, the rates of which were, as Geitel had shown, in the ratio of 3 : 2 : 1. Later work by Taylor,[5] on neutral salt action in the acid hydrolysis of triacetin, further confirms this view.

It is without doubt true that the hydrolysis of the more complex glycerides in fats and oils obeys the same rule of successive stages of hydrolysis, modified naturally by the fact that the reaction occurs in a heterogeneous medium in which, as Lowenherz[6] showed, the velocity of reaction was constant and determined by the solubility of the ester in the catalytic medium. Instances in support of this view of successive stages as applied to the fats and oils may be cited. Lewkowitsch detected the presence of dierucin in an old sample of rape oil, and the observation of Gruen and Theimer[7] on the hydrolysis of distearochlorohydrin, in which the intermediate stages of the hydrolysis of the diglyceride were isolated, is decisive proof. Detection of intermediate compounds in partly saponified fats is, however, an extremely difficult matter.

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[1] *J. pr. Chem.*, 1897 (ii.), **55**, 417; 1898, **57**, 113.

[2] *Zeitsch. Elektrochem.*, 1907, **13**, 186.

[3] *Zeitsch. physikal. Chem.*, 1906, **56**, 558.

[4] *Zeitsch. Elektrochem.*, 1907, **13**, 307.

[5] *Medd. K. Vetenskapsakad. Nobel Inst.*, 1913 (ii.), No. 31.

[6] *Zeitsch. physikal. Chem.*, 1894, **15**, 389.

[7] *Ber.*, 1907, **40**, 1801.

Hydrolysis of fats and oils by water alone is perfectly possible, though, obviously, slow in practice It was actually employed in practice in the process of R. A. Tilghmann, who caused the fat and water to be forced through a coiled pipe heated to 300°. The hydrolysis was incomplete, and destruction of the fatty matter occurred. In modern attempts to carry out hydrolysis by water alone, the use of superheated steam under pressures up to 15 atmospheres has been invoked, always, however, with the difficulty that the process is never complete.

The use of acids as catalysts has led to two distinct technical processes, the so-called Acid Process and the Twitchell Process. These may now be considered.

The acid process.--Lewkowitsch has shown that, using hydrochloric acid of sp. gr. 1·16 as catalyst, hydrolysis of fats and oils may be accelerated, but the process has not acquired technical importance as yet, since the reaction can be more readily accomplished using concentrated sulphuric acid as hydrolytic accelerator At first sight this would appear to be an anomalous result in view of the known fact that hydrochloric acid is the stronger acid of the two. It is probably explained partly on the view that hydrochloric acid does not facilitate mutual solution of fat with water and on the fact that emulsification is small with hydrochloric acid as agent Furthermore, sulphuric acid is probably effective through the formation of fatty sulphonic acids, which are doubtless stronger acids than the sulphuric acid itself, promoting, also, mutual solubility in the two phases and emulsification.

The action of sulphuric acid as hydrolytic agent was first described by Cornett in 1777. As now employed in practice, the operation is briefly somewhat as follows. The fat is first heated to 120° to free it from water and then run in the molten state into a mixing machine, in which it is thoroughly admixed with 4-6 per cent. of concentrated sulphuric acid of a gravity of 66° Bé. With acid of such strength, the subsequent hydrolytic change attains its maximum. During the process of mixing, which occupies 20-30 minutes, reaction is vigorous, the mass chars to a certain extent, and some reduction of sulphuric to sulphurous acid occurs. In this part of the process, mixtures of sulphonated fatty acids, sulphuric esters of glycerol as well as the free acids, and various products of secondary reactions are undoubtedly present After completion of this reaction, the mass is boiled with water, the free fatty acids rising to the surface and the glycerine remaining behind in the aqueous solution of sulphuric acid. It is this second stage of the process which forms the real hydrolysis.

A considerable advantage in the employment of the acid process is the increase in the yield of solid fatty acids over that attained by other processes *This has been demonstrated by Lewkowitsch to be due to conversion of a portion of the oleic acid into the solid iso-oleic acid* by a complex series of changes involving the intermediate formation of sulpho-oxystearic and oxystearic acids. This conversion is one of great technical importance, since it results in increased yields of candle material[1] The glycerine yield is smaller than that obtained by catalytic processes employing alkalis

The Twitchell process.—The importance of the catalytic agent employed, in the successful operation of a catalytic process, is beautifully demonstrated in the Twitchell process for the hydrolysis of fats and oils into glycerine and fatty acid. The Twitchell reagent also exemplifies excellently the applicability to practical problems of knowledge accumulated in the course of theoretical investigation In this particular case the theoretical knowledge did not precede the invention, since the first patent for the Twitchell process[2] was granted at a time when the attention devoted to catalytic processes was not so pronounced as it now is, and when the theoretical point of view relative to the mechanism of the process was by no means so developed as it is to-day

In an investigation of the catalytic rôle of sulphuric acid in the hydrolytic splitting of fats and oils, Twitchell observed that sulphur compounds produced by the action of the sulphuric acid upon the fat might be separated from the fatty material by suitable methods of extraction, and could readily be identified as sulphonic acids To such acids Twitchell attributed the catalytic properties observed in the Acid Process of hydrolysis Accordingly, he prepared sulpho-acids of the fatty acids, such as sulpho-stearic acid, and such reagents were the agents first employed by him for the hydrolysis Later, the accidental discovery of fatty aromatic sulphonic acids yielded the reagents which have been put to practical use in the separation of glycerol and fatty acids The original aromatic fatty sulphonic acid was made by treatment of a mixture of benzene and oleic acid with an excess of sulphuric acid On pouring the mass into water, an oily layer of the desired product resulted[3] Instead of benzene, naphthalene is used with oleic acid in the manufacture of the commercial article, and other hydrocarbons may also find application Such catalytic agents, when added in the proportion of a half per cent or less to fat boiling with water in an open tank, will cause the separation of the glycerol

The views of Twitchell in regard to the properties of a suitable catalyst for the hydrolysis of fats have been expressed in his paper, "A Reagent in the Chemistry of Fat". The catalyst should be a strong acid, highly dissociated in water, and should be soluble both in the fat to be hydrolysed and in the water It should also tend to promote the solution of one in the other It is now well known that the aromatic sulphonic acids are very strong acids, comparable in strength with strong mineral acids such as hydrochloric acid. The introduction of higher fatty radicals into the nucleus confers upon such acids the physical character of fats or oils, thereby increasing the mutual solubility, whilst at the same time yielding soapy solutions with water. The activity of the hydrolytic agent has been attributed to the emulsifying action of the reagent, promoting the formation of an intimate mixture of oil and water, thereby exposing a greater surface of action to the reagent. It must be observed that emulsification alone is not a sufficient explanation, as fats do not hydrolyse at 100° to any practical extent with water alone, even with good emulsification. It is to the presence of the strong acid and the promotion of mutual solubility as much as to emulsification that the efficient hydrolysis must be attributed.

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[1] See Lewkowitsch, *Chem Techn Oils, Fats, and Waxes*, vol 3, p 188

[2] U.S.P 601603/1897

[3] U S P 628503/1899

The first operation in the process usually consists in the removal of foreign impurities by boiling the fatty material with dilute sulphuric acid. The fat is then transferred to open wooden tanks and mixed with half its weight of water, to which is added 2 per cent of the catalytic agent. The mass is then thoroughly agitated by blowing through the system live steam from perforated coils in the tanks. Hydrolysis is complete in about an hour, after which the emulsion is destroyed by the addition of dilute sulphuric acid. Two layers separate, the fatty acid in the upper and the glycerine in the aqueous layer below.

The advantages to be gained by the use of the Twitchell process are many. In operation it is simple and the capital cost of plant required is low. It can also be employed in large units, as contrasted with the small units and heavy initial cost of earlier hydrolytic processes. The process is operated at the ordinary pressure. The process of hydrolysis is practically complete, and, for low-grade fats, it is especially suitable. In this way materials such as garbage-grease and the footings of cotton-seed oil can be employed as raw materials in the soap or candle industry, thus releasing higher-grade fats for use as food products. With low-grade materials fractional distillation of the fatty acids is necessary to improve their purity and colour. The glycerine liquors obtained are free from salts, and so the process of concentration is much facilitated. Since the product of hydrolysis is the free fatty acid, the more economical sodium carbonate can be used in place of caustic liquor in the production of soaps

The process is now extensively used, not only in America, but also in the continental European countries. The larger soap plants in Germany, Austria, Belgium, Holland, and Scandinavia operate principally with the Twitchell process. Its use in this country is increasing.

An analogous patent to the Twitchell patents has recently been obtained by Petroff in Russia. In this case the reagent employed is obtained as a by-product in the refining of petroleum with fuming sulphuric acid. The compound is a simple sulphonic acid of hydrocarbon radicals, probably not of the paraffin series It is now being largely employed as an efficient catalyst for hydrolytic splitting

Saponification of oils and fats by alkalis.—In considering the technical use of alkaline catalysts for promoting the hydrolysis of glycerides, the same general principles hold that were enunciated in the previous theoretical treatment It will be shown that the rate of saponification is directly proportional to the effective concentration of the base employed, which also determines the time and temperature conditions to be observed for completion of the hydrolysis

The technical processes concerned may be treated in two sections (*a*) saponification with the aid of alkaline earths, (*b*) saponification with the aid of caustic alkalis

Saponification with lime and magnesia. The autoclave process.—Triglycerides may be saponified completely by solutions of lime in open vats at the boiling point, provided an excess of lime be used The quantity of alkaline earth required amounts on the average to 12-14 per cent by weight of the oil This method of saponification was introduced into industry by de Milly in France Live steam is used to heat up the material in lead-lined vats, and serves also to keep the mass in a state of agitation and of intimate mixture or emulsification The calcium soap of the fatty acid is formed in the process, the glycerine remaining in the aqueous solution Decomposition of the soap is effected with the aid of sulphuric acid, the fatty acid forming a floating layer on the liquid, the precipitated sulphate separating to the bottom

The lime employed functions as a catalyst, and it is not necessary to use sufficient for complete conversion of the fatty acid to calcium salt On the other hand, if smaller quantities of lime be used the concentration of catalyst, and therefore the catalytic activity, are diminished, so that other means must be employed to accelerate the reaction This is done by carrying out the process in autoclaves under pressure In such case the temperature employed can be considerably increased beyond the boiling point of water whereby the velocity of reaction is correspondingly augmented Thus, with only 1 per cent of lime under a pressure of 12 atmospheres, corresponding with a temperature of 190°, a virtually complete hydrolysis may be effected It will be obvious that such a reduction in the quantity of lime employed is of considerable advantage in the economy of sulphuric acid required to decompose the calcium soap formed In actual practice it is customary to employ somewhat more lime than the above for the autoclave process, as the employment of high temperatures causes discoloration of the fatty acids produced Modern practice in the candle industry calls for a working pressure of 8 atmospheres, with the addition of about 3 per cent of lime The process of hydrolysis is practically complete in about eight to ten hours The reaction is rapid in the first two hours, as much as a 77 per cent conversion being obtained. In the succeeding period the percentage of hydrolysis slowly increases to a maximum of about 99 per cent at the end of the tenth hour. For soap manufacture the hydrolysis must be conducted at still lower pressures in order to avoid discoloration. A pressure of 5 to 6 atmospheres is employed and the degree of hydrolysis reaches about 80 per cent.

Magnesia and zinc oxide have also been employed as catalytic accelerators. They have the advantage that they do not yield insoluble sulphates on treatment of the fatty soaps produced in the hydrolytic process. On the contrary, owing to their less basic character, the rate of hydrolysis is not so rapid and the percentage hydrolysed not so considerable. Magnesia also shows a tendency to produce emulsions not readily discharged in the subsequent treatment. Zinc oxide with the addition of zinc dust has been used together with lime in the ordinary autoclave process. The product, it appears, is less discoloured.

Saponification with caustic alkalis. It is obvious that owing to their insolubility and the consequent high concentration of catalytic agent thereby attained, hydrolysis with caustic alkalis should be rapid and complete. Moreover, the temperature required is by no means so considerable as is required with alkaline earths. Hydrolysis of fats with caustic alkalis is the *metier* of the soap-maker. Sufficient of the hydrolytic agent is used to combine with all the free fatty acid formed to yield the sodium or potassium salts which constitute the basic material of the normal soaps of industry. Actually an excess of the alkali is always used to facilitate the hydrolytic process. There is no doubt, however, that the hydrolysis could be catalytically effected in the presence of only small amounts of such hydrolytic agents. A readjustment of time and temperature conditions would, however, be necessary.

Two processes of alkali saponification are employed in the preparation of soap, differentiated by the temperature at which the saponification is effected.

In the cold process, as the name implies, no external heat is applied. In consequence a long period of saponification is necessary. The molten fat is churned up with the requisite quantity of alkali dissolved in water sufficient in amount to give to the soap the desired degree of hardness and solubility. Reaction sets in and the mass thickens. Sufficient heat of reaction is given out to bring about further saponification in the adjacent layers, with increasing velocity owing to rise of temperature, the oil assisting by preventing dissipation of the heat. This process continues throughout the mass and is complete in twenty-four to thirty-six hours, when about 97 per cent of the glyceride has been converted into glycerine and soap. After the initial operation the conversion is effected in frames, and when saponification is complete the mass is sufficiently solid that it may be cut into slabs. Obtained in this manner, the soaps always contain a small excess of free alkali, which for many purposes is an unsuitable ingredient

Neutral soaps are obtained by means of the hot process The hydrolysis is carried out in large soap kettles The oil is brought to 80° by means of steam, which condenses to water in the system Caustic soda is then gradually added to the contents of the pan, and ebullition is brought about by further introduction of live steam In this process, also, the velocity of saponification is accelerated by the heat of reaction The quantity of caustic alkali to be used is governed by the nature of the oil to be saponified, and, when addition is complete, the separation of the soap from the glycerine liquors is assisted by salting out with common salt The subsequent operations in the hot process are concerned with the further refinement of the soap curd to ensure complete hydrolysis of the fats and a grading of the material obtained according to the soap value

FURTHER HYDROLYTIC PROCESSES

The hydrolysis of acyl derivatives.—In addition to his studies on the hydrolysis of esters in presence of acids, Ostwald[1] investigated the hydrolysis of acetamide in order to determine the relative strengths of acids, arranging these in a table of decreasing activity from hydrochloric to acetic acid Since this early work the reaction has frequently been employed in the endeavour to obtain a clearer comprehension of catalytic activity As was shown by Crocker and Lowe,[2] the reaction is catalysed by both acids and bases, the hydrolysis proceeding in every case investigated as in ester hydrolysis, more rapidly with alkalis than with acids under similar experimental conditions The rate of hydrolysis was shown to diminish in a homologous series with increasing complexity of amide Aliphatic amides are more readily hydrolysed than aromatic amides, and the influence of substitution in the benzene ring is marked[3] The reaction in both acid and alkaline solutions is bimolecular, in accordance with the equations

$$(a)\quad R.CO\ NH_2 + H_2O + HX = R\ COOH + NH_4X,$$
$$(b)\quad R\ CO\ NH_2 + H_2O + MOH = R\ COOM + NH_4\ OH$$

Crocker and Lowe showed, however, that good reaction constants were obtained if, instead of the concentration of base and acid, the ionic concentrations were substituted

Acree and Nirdlinger[4] drew the same conclusion, independently, in a study of the hydrolysis of various concentrations of aqueous acetamide, using different strength of hydrochloric acid, and suggested that it was a complex cation,

$$((CH_3 . CO . NH_2 . H),$$

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[1] *J pr Chem*, 1883, **27**, 1

[2] *J Chem. Soc*, 1907, **91**, 593, 952.

[3] Sudborough, *ibid*, 1894, **65**, 1030, 1895, **67**, 587, 1897, **71**, 229

[4] *Amer. Chem. J*, 1907, **38**, 489

which underwent hydrolysis. The ammonium chloride formed was shown to have a marked accelerating action on the hydrolysis. Added neutral salts acted similarly, the phenomenon being subsequently associated with the view that both ions and undissociated molecules may possess catalytic activity.[1]

The hydrolysis of amides of dibasic acids was investigated by von Peskow and Meyer,[2] and showed marked points of divergence from the results of Meyer with esters of dibasic acids. The values of the reaction constant obtained showed an initial steady decrease with progress of hydrolysis, and only after some time yielded steady values. The abnormality is associated with the relative values of the velocities of hydrolysis of the two amide groupings. The researches on dibasic esters showed that an apparent unimolecular reaction constant was explainable on the assumption that the reaction constants of hydrolysis of the two groupings were in the ratio 2 : 1 (see p. 56). It was shown that with the amides in acid hydrolysis k_1 is smaller than k_2, whereas with alkalis k_2 is the smaller. This was assumed to be connected with a repulsion between the negatively charged acid amide radical ($NH_2 . OC . R . CO . O'$) and the negatively charged OH' grouping, whereas in the acid reaction an attraction to the hydrogen ion would ensue.

The hydrolysis of imido esters. — Important conclusions with reference to the catalytic action of acids in a variety of hydrolytic processes have been obtained by Stieglitz and his co-workers[3] in investigations of the reactivity of imido esters with water and ammonia. An imido ester such as methyl imido benzoate is slowly decomposed by water, one of the decompositions resulting therefrom being the formation of ammonia and methyl ester:

$$C_6H_5C(NH)OCH_3 + H_2O = NH_3 + C_6H_5CO_2CH_3.$$

The addition of an acid, for example hydrochloric acid, enormously accelerates the change. It was shown that the acceleration was due to the fact that the reacting component in this decomposition is the positive ion of the ester, as expressed in the equation

$$C_6H_5(:NH_2{}^{+})OCH_3 + H_2O = C_6H_5CO_2CH_3 + NH_4{}^{+}.$$

Acceleration by neutral salts, entirely analogous to the "salt effect" in the catalysis of esters by acids, was found also in these reactions. This salt effect allowed for, the reaction could be expressed by an equation of the form

$$\frac{dx}{dt} = K_{\text{ion}} \times C_{\text{pos est. ion}} \times [C_H \times C_{OH}].$$

Applied to the saponification of ordinary esters, the main difference resulting is that for such exceedingly weak bases as esters the concentration of the positive ester ion is practically proportional to the concentrations of ester and hydrogen ion present at any moment, so that the above equation becomes

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[1] Acree, *Amer. Chem. J.*, 1912, **48**, 352 *et seq.*

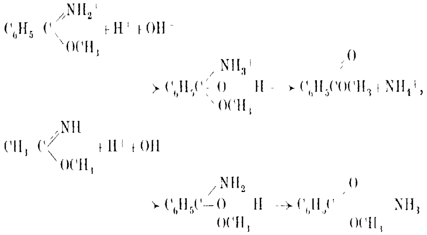
[2] *Zeitsch. physikal. Chem.*, 1913, **82**, 129.

[3] For summaries of this work, see *J. Amer. Chem. Soc.*, 1910, **32**, 221; 1913, **35**, 1774.

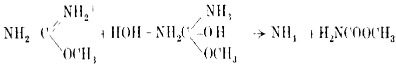
$$\frac{dx}{dt} = K \times C_{ester} \times C_{H} \times [C_{H} \times C_{OH}],$$

which is in agreement with common experience

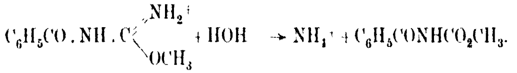
Stieglitz propounds the question as to why the reaction with the ion should be enormously faster than the entirely analogous possible action of water on the non-ionised free ester The two reactions may be expressed, in agreement with experimental results, in a series of stages for the two cases



Stieglitz concludes that the accelerating or catalytic effect of the acid is most intimately associated with the transformation of the positive ion of a weaker base into that of a stronger base For, as emphasised by Stieglitz, whereas the imido esters are rapidly hydrolysed by water in the presence of acid, this is not the case for the closely related compounds the urea ester salts, which structurally considered, should react with water, but are quite stable in acid solution The transformation,



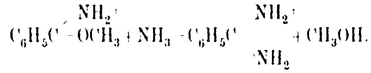
only takes place to a very slight extent at 100° C and, at ordinary temperatures, where imido ester salts are completely hydrolysed in one to ten hours, the urea ester salts have not been observed to decompose at all In this case we have the notable fact that such a transformation would involve the change of a salt of a stronger base into that of a much weaker one an ammonium salt and this does not take place Stieglitz tested this view with the benzoyl urea esters, which form much weaker bases than ammonia They ought to be hydrolysed in acid solution, according to this view, as smoothly as imido esters This is actually the case; urethanes and ammonium salts readily result according to the equation



$$C_6H_5CO.NH.C\begin{cases}NH_2^+\\ OCH_3\end{cases} + HOH \rightarrow NH_4^+ + C_6H_5CONHCO_2CH_3.$$

It is apparent that this transformation of the ion of a weaker base into that of a stronger is no doubt the result of the decrease in free energy involved in the union of the acid with the stronger base.

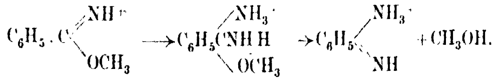
The several factors of interest obtained by Stieglitz and his co-workers in these studies of hydrolysis of imido esters received beautiful confirmation by his further studies of the interaction of ammonia and imido esters whereby amidines result:



$$C_6H_5C\overset{NH_2^+}{-}OCH_3 + NH_3 \rightarrow C_6H_5C\begin{cases}NH_2^+\\ NH_2\end{cases} + CH_3OH.$$

The action is accelerated by acids and by addition of salts just as in the hydrolysis, and it was shown that again it was the positive ester ion which underwent change. Whereas, however, urea esters would not react with water in acid solution because the salt of a stronger base would thereby be converted to that of a weaker, this is not true when ammonia is the reactant. Reaction of urea esters with ammonia produces guanidines, which are stronger bases than the urea esters themselves. The guanidines, therefore, according to theory, are produced readily from urea esters and ammonia, in presence of acids, the positive ester ion again being the rapidly reacting constituent.

The kinetic studies of the interaction of imido esters and ammonia were not inconsistent with the assumption that reaction occurred between the ester and ammonium ion rather than between the ester ion and ammonia. The answer to the query as to which mechanism is correct is supplied by preparative organic chemistry. In place of ammonia, primary and secondary amines may be employed. Pinner found, however, that tertiary amines do not form amidines with imido esters.[1] Were the reaction between the amine ion NHR_3^+ and the ester, this should be quite possible. The alternative would not be possible, as the following equation, showing the mechanism assumed by Stieglitz, makes quite evident:



$$C_6H_5.C\begin{cases}NH^+\\ OCH_3\end{cases} \longrightarrow C_6H_5C\begin{cases}NH_3^+\\ NH\,H\\ OCH_3\end{cases} \rightarrow C_6H_5C\begin{cases}NH_3^+\\ NH\end{cases} + CH_3OH.$$

The applicability of Stieglitz's conclusion that the actions accelerated by acids are changes from a weaker base to a stronger may now be considered in reference to the reversible process of ester hydrolysis and esterification in presence of acids. According to the Stieglitz principle, in the hydrolysis the salt of the weaker ester oxonium base *forms the salt (ion) of the stronger alcohol oxonium base In the esterification the salt of the weaker organic acid oxonium base forms* the salt of the stronger ester oxonium base. This latter conclusion is not that reached by Goldschmidt, who concluded that the reaction was between the oxonium ion of the alcohol and the organic acid Both alternatives give the same kinetic expression It is the work of Stieglitz on imido esters which gives the preference to his point of view.

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[1] *Imidoæther*, pp. 86, 89 (1901).

Similarly in the production of oximes from hydroxylamine and ketones, in the presence of acids, Acree[1] concluded originally that the reaction was probably between a cation of hydroxylamine and the ketone Later, he pointed out that his data would agree equally well with the assumption that the hydroxylamine reacts with the oxonium ion of the acetone[2] This latter is in agreement with Stieglitz's principle, the change being from the exceedingly weak oxonium base of the ketone into the ion of the much stronger base, the oxime

The hydrolysis of ethers and acetals.—Reasoning from the well-known dehydration of alcohols in the presence of sulphuric acid to yield ethers, one would anticipate the reverse production of alcohols by hydrolysis of ethers in presence of acids This actually occurs, as was shown by Erlenmeyer[3] and Lieben[4] Pease and Yung[5] have recently established the reversibility of the process, for ethyl alcohol and diethyl ether, using both sulphuric acid and alumina as catalysts, with the former at 130° and with the latter at 275° The values of the equilibrium constants are 8·0 and 0·66 respectively From such equilibrium measurements they have accordingly deduced the free energy data for the reaction and for the formation of ether vapour

Acetals are mixed ethers derived from alcohols and the unstable glycols of which aldehydes and ketones are the anhydrides They are hydrolysed by dilute acids Their reactivity in the presence of such acid solutions has recently been studied by Skrabal and his co-workers[6] and compared with that of diethyl ether Thus, with unit concentration of acid catalyst and with the minute as the unit of time the following data were obtained, in these kinetic studies, for the unimolecular constant·

Diethyl ether .	0·0000006	Ethyl acetal of acetaldehyde	30
Methyl acetal of formaldehyde	0·000765	Ethyl ether of orthoformic acid	23000
Ethyl acetal of formaldehyde	0·00468	Ethyl ketal of acetone	75000
Cane sugar . .	0·01	Ethyl ether of orthoacetic acid	330000

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[1] *Amer Chem J*, 1907, **38**, 308

[2] *Amer Chem J*, 1908, **39**, 302

[3] *Zeitsch f Chemie*, 1868, **4**, 343.

[4] *Annalen*, 1873, **165**, 136

[5] *J Amer Chem Soc.*, 1924, **46**, 2397

[6] Skrabal and Ringer, *Monatsh*, 1921, **42**, 9, Skrabal and Schiffrer, *Zeitsch. physikal. Chem.*, 1921, **99**, 290, Skrabal and Airoldi, *Monatsch.*, 1924, **45**, 13; Skrabal and Baltdschiens, *Monatsh*, 1924, **45**, 19

In the hydrolysis of the ethyl ether of ortho-acetic acid it was shown that the reaction takes place in two stages:

$$(a)\quad CH_3C(OC_2H_5)_3 + H_2O = CH_3COOC_2H_5 + 2C_2H_5OH,$$
$$(b)\quad CH_3COOC_2H_5 + H_2O = CH_3COOH + C_2H_5OH.$$

In alkaline solution (*a*) is slow, independent of the hydroxyl ion concentration, and therefore a water hydrolysis The reaction (*b*) is relatively fast in such solutions. In acid media (*a*) is fast and (*b*), relatively, is slow. It was shown that in a primary and secondary phosphate buffer solution the constants for (*a*) and (*b*) were respectively $k_a = 0{\cdot}052$ and $k_b = 1{\cdot}34 \times 10^{6}$. These results lead to an expression for the total effect of the form

$$\frac{dx}{dt} = k_w(a - x) + k_s[H^{\cdot}][a - x],$$

where $k_w = 5{\cdot}7 \times 10^{-4}$ and $k_s = 1{\cdot}0 \times 10^{6}$. It is evident, therefore, that the hydrolysis of such bodies can only be accomplished very slowly in water or alkaline solutions, but, on the contrary, are readily hydrolysed by acids. In this respect the acetals are readily distinguished from ordinary esters.

Skrabal, Pfaff, and Airoldi have also shown recently[1] that keto carbonic esters are much more rapidly hydrolysed in alkaline media than in acid media, thus conforming to the normal ester type. Thus the following data were obtained in acid and alkaline solutions:

	k acid.	k alkaline
$CH_3COCOOC_2H_5$ . . .	0·00816	$1{\cdot}1 \times 10^{5}$.
$CH_3CO . CH_2CH_2COOC_2H_5$.	0·00156	7 7

It will be noted that the positional influence of the keto group is very marked on the relative rates in the two media.

Hydrolysis of halogenated organic acids. A well-investigated mechanism of hydrolytic acceleration is to be found in a study of the hydrolysis of halogen acetic acids and their sodium salts. The hydrolysis of chloroacetic acid by hot water proceeds quantitatively, according to the equation

$$CH_2Cl . COOH + H_2O = CH_2 . OH . COOH + HCl,$$

and the reaction is unimolecular,[2] even with wide variation of the initial acid concentration.[3] The reaction is not greatly affected by hydrogen chloride, formed or added, or by the addition of neutral salts such as sodium chloride in normal solution.

The hydrolysis of neutral sodium chloroacetate in dilute solution was shown by Senter to be unimolecular with slight deviations in normal solutions. The rate of reaction is diminished by certain neutral salts In presence of alkali, the reaction is bimolecular in dilute solution, and may be formulated by the equation

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[1] *Monatsh.*, 1924, **45**, 141.

[2] Schwab, van 't Hoff, *Studien zur chemischen Dynamik.*

[3] Senter, *J. Chem. Soc.*, 1907, **91**, 461.

$$CH_2Cl\cdot COONa + NaOH = OH\cdot CH_2\cdot COONa + NaCl$$

This reaction, however, is accelerated by the addition of neutral salts, in marked contrast to the influence of such salts on the alkaline hydrolysis of esters The accompanying table shows the effect of a series of neutral salts on the velocity of the hydrolytic processes occurring (*a*) in a solution of *N*/10-sodium bromoacetate and *N*/10-sodium hydroxide, (*b*) in a solution of *N*/40-ethyl acetate and *N*/40-sodium hydroxide [1]

Neutral Salt	Increase per cent of Velocity Coefficient in Reaction (*a*)	Increase or Decrease of Velocity Coefficient per cent in (*b*)
N/1 Sodium nitrate		19
,, chlorate	51	12
,, sulphate		12
,, ferrocyanide	+53	0
,, benzenesulphonate	51	
,, benzoate	+51	100
,, formate	+100	+3
,, acetate	102	0
,, tartrate	+98	8

A careful series of investigations of the great activity of neutral salts of organic acids in the former reaction as compared with that in alkaline ester hydrolysis showed that the activity was closely associated with the mechanism of the reaction The effect was traced [2] to the intermediate formation of sodium acetoxyacetates, as exemplified in the equation

$$CH_2Br\cdot COONa + CH_3\cdot COONa = CH_3\cdot CO\cdot O\cdot CH_2\cdot COONa + NaBr,$$

which compounds are hydrolysed by alkali as fast as formed In neutral solution the compounds are hydrolysed slowly set the tempo of the reaction, and determine the influence of neutral salts in such solutions

Senter and Ward, in connection with this work, also investigated the hydrolysis of acetoxyacetic acid and its salts in neutral, acid, and alkaline solutions It was shown that the hydrolysis of the acid was catalysed by hydrogen ions either autocatalytically with ions from the acid itself or from added acids The hydrolysis of the acid is ten times as rapid as that of the sodium salt under similar conditions, doubtless due to the absence of the accelerating hydrogen ions In alkaline solution the acceleration was enormous, the effect of *N*/10-sodium hydroxide being to speed up the reaction to 100,000 times its velocity in aqueous solution.

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[1] Senter and Bulle, *J Chem Soc* 1912 **101**, 2528

[2] *Loc cit*, and Senter and Ward, *J Chem Soc*, 1912, **101**, 2534

The hydrolytic decomposition of the bromo-substituted organic acids exhibits an interesting case of inhibition, the hydrobromic acid formed in the reaction retarding the velocity of reaction, so that the constants calculated for a unimolecular reaction show a continuous decrease. Müller[1] formulated this inhibitory effect of hydrobromic acid in the hydrolysis of bromosuccinic acid, assuming the reaction velocity to be proportional to the unchanged bromosuccinic acid and inversely to that of the hydrobromic acid formed, thus obtaining an equation of the form

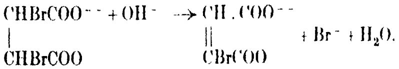
$$\frac{dx}{dt} = k\frac{(a - x)}{(x)},$$

which gave satisfactory agreement with experimental results.

Senter[2] showed that in the hydrolytic decomposition of bromopropionic acid the reaction mechanism was not so simple as that assumed in the case of bromosuccinic acid. With the assumption that both the non-ionised acid and the $CH(CH_3)BrCOO'$ ions undergo change, each at their own definite reaction velocities, Senter and Porter[3] successfully interpreted the experimental results. The inhibitory influence of the hydrobromic acid would, on this view, be due to the suppression of the ionisation of the bromopropionic acid, calculation showing that in this particular case the velocity constants of hydrolytic decomposition of ion and undissociated acid were $k = 0{\cdot}030$ and $k_2 = 0{\cdot}00053$ respectively.

Neutral salt action in the hydrolysis of halogenated compounds: cation catalysis.—Consideration may now be given to the investigations of Holmberg on the hydrolysis of halogenated organic compounds in alkaline solutions in presence and absence of neutral salts. These researches are of importance in the general problem of salt catalysis, since marked variations in catalytic behaviour of the salts are shown in the different examples. Furthermore, as Bronsted[4] has recently shown, these variations are in accord with the ideas developed by him towards a general activity theory of neutral salt action.

Holmberg first studied[5] the reaction between alkalis and dibromsuccinic acid, a reaction which, stoichiometrically and kinetically, proceeds according to the scheme



$$\begin{array}{l} CHBrCOO^{--} \\ | \\ CHBrCOO \end{array} + OH^- \rightarrow \begin{array}{l} CH.COO^{--} \\ || \\ CBrCOO \end{array} + Br^- + H_2O.$$

The velocity constants of the process, at varying concentrations of the reactants and also in presence of salts, show a marked dependence on the total ionic concentration, as is evident from the subjoined table for sodium as cation.

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[1] *Loc. cit.*, and Senter and Ward, *J. Chem. Soc.*, 1902, **41**, 483.

[2] *J. Chem. Soc.*, 1909, **95**, 1836.

[3] *Ibid.*, 1911, **99**, 1049.

[4] *Zeitsch. physikal. Chem.*, 1922, **102**, 169.

[5] *Zeitsch. physikal. Chem.*, 1912, **79**, 147.

m_{SNa_2}	m_{NaOH}	m_{NaCl}	m_{NaNO_3}	$m_{Na_2SO_4}$	C_i	k
0·01222	0·01222				0·036	1·51
0·01727	0·01727				0·051	1·64
0·02473	0·02473				0·074	1·85
0·03109	0·03109				0·093	1·85
0·02154	0·02154		0·0313		0·096	2·08
0·02154	0·02154			0·0164	0·097	2·13
0·02473	0·02473	0·0354			0·110	2·11
0·03753	0·03753				0·113	2·07
0·04504	0·02252				0·113	2·19
0·02815	0·05630				0·113	2·19

The first and second columns record the concentrations of sodium dibromsuccinate and sodium hydroxide used, the third, fourth, and fifth those of sodium chloride, nitrate, and sulphate. In the sixth column is the total cation concentration, and, in the seventh, the corresponding velocity constant.

Holmberg called this phenomenon cation catalysis, since the velocity, with unchanged cation, appears to depend wholly on the total ion concentration, not upon the nature of the anions present. Holmberg showed, in accord with this, that variation of the cation, especially a change to calcium and barium salts, produced a profound change in velocity, an extraordinary acceleration with the divalent cations.

Bronsted shows that these results are quite in agreement with his activity theory of salts, applied to reaction velocity. He formulates the reaction measured by means of the equation

$$S^{--} + OH^{-} \longrightarrow (S \cdot OH)^{---},$$

where S refers to the dibromsuccinic, OH^- to the hydroxyl ion, and $(S \cdot OH)^{---}$ to a trivalent complex formed by the association of the two anions. Applying Bronsted's activity theory of reaction velocity, the velocity should therefore be

$$v = k \times (C_{S^{--}}) \times (C_{OH^-}) \times \left(\frac{f_2 f_1}{f_3}\right),$$

where f_1, f_2, and f_3 refer to the activity coefficients of the several ions, subscripts indicating valencies of the ions. From Bronsted's solubility studies, he concludes that the activity factor varies in the ratio 1 : 1·8 for a change from 0·02 normal to 0·10 normal solutions. The velocity data for sodium salts in this range yield a value of 1·6. The independence of anion shown by the velocity measurements is also in agreement with Bronsted's theory, since the activity factor is determined in dilute solution largely by the valence and not by the nature of the ion. Furthermore, Brönsted's solubility studies have shown that as regards the activity coefficient, at the same equivalent concentration, a divalent cation will influence a divalent anion more pronouncedly than will a univalent ion, and that this holds true to an even greater degree for a trivalent ion. Hence the enhanced effect of barium and calcium ions in Holmberg's measurements, which effect, however, is more pronounced than Bronsted would anticipate from solubility data.

The success of the Brönsted theory when applied to neutral salt catalysis is apparent when the second research of this series by Holmberg[1] is considered. In this case the alkali decomposition of α-β dibrompropionic acid and α-β dibrombutyric acid was measured. In this case it was found that the ratio $\frac{k_{0 \cdot 1}}{k_{0 \cdot 02}}$, the ratio of the velocity constants in 0·1 and 0·02 normal solutions, had a value of 1·21 as compared with a value of 1·8 in the previous example. The similarity of the two sets of reactions would lead one to expect a similar salt effect. Brönsted indicates the difference between the two examples by pointing out that whereas the case already considered involves a divalent halogenated anion, this second research involves a univalent anion, whence the reaction measured becomes

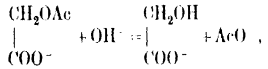
$$A \ + OH^{-} = (A\,.\,OH)^{--},$$

and, as a consequence, the reaction velocity expression becomes

$$v = k \times C_{A^{-}} \times C_{OH^{-}} \times \frac{f_1^{2}}{f_2}.$$

For such a system, from activity theory, a value for $\frac{f_1^{2}}{f_2} = 1 \cdot 22$ is theoretically calculable, in agreement with the observations recorded.

Similarly, for a later research of Holmberg,[2] the hydrolysis of acetyl glycollic acid:



$$\begin{array}{l} CH_2OAc \\ | \\ COO^{-} \end{array} + OH^{-} = \begin{array}{l} CH_2OH \\ | \\ COO^{-} \end{array} + AcO^{-},$$

the reaction type is exactly analogous to the preceding case, and so the same salt effect, $\frac{k_{0 \cdot 1}}{k_{0 \cdot 02}} = 1 \cdot 22$, should be, and is, found. The alkali hydrolysis of iodo-acetic acid also showed[3] a positive salt action, as would be expected from the equation

$$CH_2ICOO^{-} + OH^{-} = CH_2OHCOO^{-} + I^{-}.$$

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[1] *Zeitsch. physikal. Chem.*, 1912, **80**, 573.

[2] *Zeitsch. physikal. Chem.*, 1913, **84**, 451.

[3] *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, Nr. 11.

The conversion of iodo-acetic acid into sulpho-cyan-acetic acid[1] showed interesting results. In neutral solution the reaction showed the normal salt effect which would be expected from the equation

$$CH_2ICOO^- + CNS^- = CH_2(CNS)COO^- + I^-$$

The ratio $\frac{k_{0·1}}{k_{0·02}}$ was, in the mean, 1·29. Further, the ratio $\frac{k_{Ba^{++}}}{k_{Na^+}}$ was approximately 1·2. The reaction conforms to a velocity equation of the form

$$v = k \times C_{CH_2ICOO^-} \times C_{CNS^-} \times \frac{f_1^2}{f_2}$$

In strong acid solution, on the contrary, where the dissociation of the iodo-acetic acid is practically suppressed, the reaction must be, primarily,

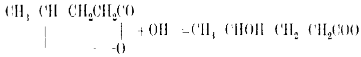
$$CH_2ICOOH + CNS^- = CH_2(CNS)COOH + I^-$$

On Bronsted's activity theory this would give a velocity equation of the form

$$v = k \times C_{CH_2ICOOH} \times C_{CNS^-} \times f_0,$$

in other words, the normal reaction process, Bronsted's Type 0. Actually, and in complete agreement with this view, Holmberg found a velocity constant practically independent of acid and total ion concentration, although this latter was varied sixfold and the former fourfold.

Hydrolysis of lactones.—Henry,[2] and later Holmberg,[3] showed that the hydrolysis of γ-lactones by alkalis occurs according to the reaction equation

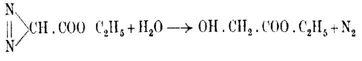


$$CH_3 . CH . CH_2CH_2CO\text{—O} + OH^- = CH_3 . CHOH . CH_2 . CH_2COO^-$$

It should, therefore, on Bronsted's theory, show no neutral action, and this was found by both the authors concerned.

The fidelity with which the Bronsted theory, as here indicated, interprets the varied manifestations of neutral salt effect in these several reactions, as contrasted with the complete inability of other theories to interpret so varied a behaviour merits, for the theory, the closest attention and consideration of the student of homogeneous catalytic action.

The diazo-ester reaction.—It was shown by Curtius[4] in 1883 that the diazo esters interacted with water with evolution of nitrogen and formation of hydroxy-derivatives of the ester residue as exemplified by the equation



$$N_2{>}CH . COO . C_2H_5 + H_2O \longrightarrow OH . CH_2 . COO . C_2H_5 + N_2$$

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[1] *Zeitsch physikal Chem*, 1921, **97**, 134

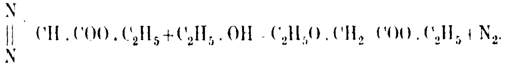
[2] *Ibid*, 1892, **10**, 96

[3] *Ibid*, 1912, **80**, 587

[4] *J pr Chem* (II), 1883, **38**, 401

The reaction is therefore a hydration process accompanied by decomposition of the molecule. As would be anticipated from the previous examples of hydration processes, Bredig and Fraenkel[1] showed that the reaction was catalytically accelerated by the presence of acids. By a study of the reaction velocity in the presence of a widely varied series of acids as well as with mixtures of acetic acid and sodium acetate, they demonstrated a close proportionality between hydrogen-ion concentration and the rate of evolution of nitrogen. The extreme sensitivity of the reaction to hydrogen ions was made use of in a succeeding investigation of Spitalsky,[2] who determined with its aid the degree of hydrolysis of potassium dichromate. With this method it could be shown that in a dilute solution containing 0·0169 mol. of the dichromate per litre, the hydrogen-ion concentration of the chromic acid produced by hydrolysis was 0·000098 mol. per litre. An even more striking application of the sensitivity of the reaction was made by Walker and Cumming,[3] who applied the diazo method to the determination of the hydrion concentrations of amphoteric electrolytes, excellent experimental agreement being obtained between the values obtained and those calculated by Walker. Thus, for a $N/32$ anthranilic acid solution, the found and calculated values were respectively $C_H = 0{\cdot}000275$ and $0{\cdot}00027$.

If the diazo-ester decomposition occurs in alcoholic solution, the ester splits off nitrogen and adds on a molecule of alcohol, which change may be represented by the equation



$$\begin{matrix} N \\ \| \\ N \end{matrix} CH.COO.C_2H_5 + C_2H_5.OH = C_2H_5O.CH_2.COO.C_2H_5 + N_2.$$

This reaction is also markedly sensitive to the presence of hydrogen ions, and can be used, likewise, for the determination of hydrion concentration in alcoholic solutions. In working out the process, Bredig and Fraenkel[4] noted the retarding influence of small quantities of water on the reaction velocity, in many aspects similar to that observable in esterification processes in alcoholic solution, extended treatment of which is given in the succeeding chapter (p. 367). The researches of Bredig, Millar, and Braune[5] demonstrated the analogy between the results in the two reactions, even to numerical agreement in the calculations of the hydrolytic constant of the hydrogen-ion alcoholate assumed by Goldschmidt to be the active catalytic agent (*vide* p. 369). Millar was able to show not only that addition of water decreased the velocity of decomposition in alcoholic solution, but also that alcohol decreased the velocity of decomposition in aqueous solution. The appended table illustrates this fact with a picric-acid concentration of 0·000909 mol. per litre as catalyst in each solvent medium.

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[1] *Zeitsch. physikal. Chem.*, 1907, **60**, 202.

[2] *Zeitsch. anorg. Chem.*, 1907, **54**, 265.

[3] *Zeitsch. physikal. Chem.*, 1907, **57**, 578.

[4] *Loc. cit.*

[5] *Zeitsch. physikal. Chem.*, 1913, **85**, 129, 170.

Grms Alcohol per 100 grms of Reaction Mixture	k_{25}	Mols of Water per litre	k_{25}
0	0.0356	0	0.057
3.31	0.0320	0.16	0.033
6.69	0.0289	0.64	0.018
14.2	0.0204	2.56	0.0064
21.9	0.0133	5.12	0.0044
		10.24	0.0049
		15.36	0.0070

The minimum value for k occurs at a concentration of 6 mols of water per litre, or at a water concentration of 11 per cent. This inhibitory influence of each on the other is extremely interesting and important in respect of the theoretical interpretation. Goldschmidt's esterification hypothesis seems scarcely applicable, without modification, to the present case, since it assumes non-activity of the free ion and ion-hydrate, an assumption scarcely consonant with the marked catalytic activity displayed by acid catalysts in decomposition of diazo esters in aqueous solution. The influence of neutral salts with a common anion on the catalytic activity of the acids was studied by Snethlage,[1] who showed that the experimental results obtained were in harmony with the theory that the undissociated molecule of the catalysing acid possessed catalytic activity. The results, however, may also be ascribed to the varying catalytic activity of free and hydrated hydrogen ions.

Bronsted and Teeter[2] have recently initiated studies of the salt effect in diazo-ester decomposition. They point out that the reaction may be looked upon as a bimolecular reaction involving the ester molecule and the hydrogen ion. As the first of these is neutral, no salt effect is to be expected when the hydrogen ions come from a strong acid. If, on the other hand, the hydrogen ion comes from a weak electrolyte, a secondary salt effect may be expected.

The process of electrolytic dissociation may give rise to the formation of ions of opposite sign, as in the following instances

$$CH_3COOH \longrightarrow H^+ + CH_3COO^-$$

and

$$TH^- \longrightarrow H^+ + T^{--},$$

where the latter equation represents the second dissociation of tartaric acid. In such cases addition of salts, in dilute solution, always increases the dissociation, since in the equilibrium equations

$$K_a = \frac{C_{Ac^-} \times C_{H^+}}{C_{HAc}} f_1^2, \quad K_a = \frac{C_{T^{--}} \times C_{H^+}}{C_{TH^-}} f_2,$$

where Ka, the thermodynamic mass action constant, is a true constant at constant temperature, and f_1 and f_2, the activities involved, are both decreasing with increasing ion concentration.

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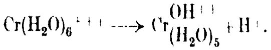
[1] *Zeitsch. physikal. Chem.*, 1913, **85**, 238.

[2] *J. Physical Chem.*, 1924, **28**, 579.

On the other hand, electrolytic dissociation may take place with no change in the total number of electric charges, as exemplified in the dissociation of the ammonium ion :

$$NH_4^+ \longrightarrow NH_3 + H^+,$$

or the hexa-aquo chromic ion :



$$Cr(H_2O)_6^{+++} \dashrightarrow Cr\overset{OH^{++}}{\underset{(H_2O)_5}{}} + H^+.$$

The thermodynamic mass action law gives here

$$Ka = \frac{C_{NH_3} \times C_{H^+}}{C_{NH_4^+}}\,;\; Ka = \frac{C_{x^{++}} C_{H^+}}{C_{y^{+++}}} \cdot \frac{f_1 f_2}{f_3},$$

where x^{++} and y^{+++} indicate the respective di- and trivalent ions, f_1, f_2, and f_3 the several activity coefficients of the ions. The dissociation of ammonium ion is, hence, little affected by addition of neutral salts. In the case of the chromic ion equilibrium, the salt addition must cause a decrease in the dissociation, because $\frac{f_1 f_2}{f_3}$ increases with increasing concentration.

These conclusions from the activity theory have been verified by Brönsted and Teeter by studying salt effect in the decomposition of diazo-acetic ester in acetic-acid solutions and in solutions containing the hexa-aquo chromic ion. In each case potassium nitrate was the added salt. In agreement with the premises, a positive salt effect was obtained with acetic acid and a negative effect with the hexa-aquo chromic nitrate.

ALCOHOLYSIS

The hydrolytic process may be generalised for all compounds containing the hydroxyl group by means of the equation

$$RCOOR' + R''OH \rightleftarrows R'OH + RCOOR''.$$

When R'OH and R''OH are two alcohols the process may be termed alcoholysis, a designation due to Haller. The process is also spoken of as ester exchange.

As with normal hydrolytic processes, strong mineral acids are active catalytic agents. In agreement with the higher efficiency of alkalis or hydroxyl ions as catalysts, it was found by Reid[1] that sodium ethylate was an even more efficient catalyst than hydrochloric acid. The reaction is reversible and equilibrium is established dependent on the concentrations of the two alcohols and their respective affinities for the ester acid.

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[1] *Amer. Chem. J.*, 1911, **45**, 506.

Haller[1] showed the applicability of alcoholysis to the replacement of complex alcohols, such as glycerine, by simple alcohols, such as methyl alcohol, in fats and oils, as, for example, cocoa butter, castor and linseed oils. His observations were made with hydrogen chloride as catalyst. His work constitutes an amplification of early observations, with the same reaction in ethyl alcohol containing hydrogen chloride, recorded by Rochleder[2] and Berthelot[3]. The exchange, in the case of polyhydric alcohols, may be stopped at intermediate stages, whereby partially esterified glycols and glycerols are obtained.

[1] *Compt. rend.*, 1906, **143**, 657, 803; 1907, **144**, 462; 1908, **146**, 259.

[2] *Annalen*, 1846, **59**, 260.

[3] *Ann. Chim. Phys.*, 1851 (iii.), **41**, 311.

CHAPTER XII

DEHYDRATION

THE removal of the elements of water from a compound or compounds with simultaneous production of a new substance is one of the earliest types of reaction studied from the catalytic point of view. The dehydration of alcohol by means of sulphuric acid, yielding ether or ethylene, forms one of the classical examples of reaction in homogeneous liquid systems from the theoretical point of view, whilst possessing a technical importance no less great in the processes of organic synthesis. There will be shown in the succeeding pages the wide applicability of catalytic dehydration processes operated both in homogeneous and in heterogeneous systems. The reactions comprise the production of ethers and hydrocarbons by dehydration of alcohols, the production of esters by removal of the elements of water from an alcohol and an acid, as well as processes of dehydration in which are produced compounds as varied as aldehydes, ketones, lactones, anhydrides, amides, thiols, and many others.

Dehydration of alcohols to form ethers. The production of ether from alcohol and sulphuric acid at 140° is an example frequently cited in evidence of the fact that a small quantity of the catalytic substance is capable of accelerating the transformation of considerable quantities of the reacting substances. Further, the explanation of the mechanism of the process by Williamson in 1851, based upon the intermediate formation of ethyl sulphuric acid, is at once a classical and splendid example of the rôle of the intermediate compound in many catalytic processes. It is demonstrable that alcohol and concentrated sulphuric acid may react together to yield an acid ester, ethyl sulphuric acid, and water, according to the equation

$$C_2H_5 . OH + H_2SO_4 \rightleftarrows C_2H_5O . SO_3H + H_2O,$$

the products being stable in the cold in presence of excess of alcohol. At 140°, however, the ethyl sulphuric acid is capable of combining with further quantities of alcohol to produce ethyl ether with the simultaneous regeneration of sulphuric acid, as follows:

$$C_2H_5O . SO_3H + C_2H_5 . OH \rightleftarrows (C_2H_5)_2O + H_2SO_4.$$

If the whole process be conducted, *ab initio*, at 140°, ether distils off uninterruptedly if alcohol be supplied continuously to the system, and, theoretically, the process might continue indefinitely. Actually, in practice, dilution of the acid with water and its partial reduction to the lower state of oxidation by side reactions cause the process of etherification finally to cease.

Ethyl sulphuric acid is capable of decomposing at higher temperatures into ethylene and sulphuric acid, which latter may again react with alcohol and yield further quantities of ethylene.

$$C_2H_5O\ SO_3H \longrightarrow C_2H_4 + H_2SO_4$$

This, therefore, is a parallel catalytic process to the above, and predominates at temperatures of 160°-170°, though naturally it must occur to some extent at the lower temperature of etherification. It will be obvious also that the attainment of successful yields in the production of ether is dependent to a degree on the avoidance of the secondary reaction yielding ethylene.

The production of ether on the technical scale is one of considerable importance, since ether functions as a solvent in many technical processes, more especially those connected with the manufacture of explosives and the organic chemical industry. Some details of the process as operated may therefore be given.

The original types of plant were adaptations of the laboratory methods of preparation to the condition of technical operation. Definite mixtures of alcohol and sulphuric acid were distilled from suitable containers, and the disappearance of alcohol by conversion into the reaction products was compensated for by continuous addition. The distillate subsequently underwent processes of purification whereby the secondary products of reaction were removed, the final rectification being a process of fractional distillation. The process as thus conducted was cumbersome in detail, and ill designed to meet requirements for large output. Such plant, therefore, has given place to designs more adapted to the needs of the various industries concerned. Actually, in the reorganisation, the type of catalytic reaction has been changed from a reaction in homogeneous liquid system to one between alcohol vapour and the liquid catalytic agent, sulphuric acid of a definite concentration maintained at a fixed temperature in the neighbourhood of 140°. The alcohol is vaporised in a series of preheaters and passes thence directly into the catalyst medium. Reaction occurs with evolution of heat, so that it is necessary to cool the sulphuric acid by means of tubes immersed in the liquid through which cold water is flowing. The products of reaction, ether and water, together with a certain quantity of unchanged alcohol, pass away from the catalyst in the form of vapour, directly to a dephlegmator in which the constituents of the mixture are fractionally condensed. At the lowest exit from the fractionating column, the water is removed. At a highe level, pure alcohol is drawn off and returns to the incoming system, whilst at the highest point in the system the ether is condensed and removed. Owing to the fact that the ether vapour travels before final condensation through the vapour of absolute alcohol, the ether obtained is very efficiently dehydrated. Ether of the highest grade of purity is thus obtained in a one-stage continuous operation. The product is so pure that it has been stated to be better than that obtainable in the laboratory with the best refinements of working. The overall yield of the process in ether is practically quantitative, a trustworthy figure quoting more than 97 per cent. conversion of alcohol to ether. The percentage of the inflowing alcohol converted in one operation amounts to 75, the residue flowing back, as mentioned, from the fractionating column to the inflowing alcohol. In the operation of the improved system, side reactions are practically completely eliminated, whilst, since the water is removed in the resultant vapour phase, dilution of the catalytic medium is obviated

As catalytic agent, various acids other than sulphuric have been suggested and employed. Phosphoric acid has found use in this manner,[1] as it is more difficultly reduced than sulphuric acid and so may have a longer period of activity. Similarly, a recent process of Kraft employs benzenesulphonic acid for the preparation of ethyl ether and other members of the series, and other aromatic sulphonic acids may be employed in like manner. However, it may safely be stated that their use is unnecessary in the light of the information recorded above as to operation with sulphuric acid. Anhydrous zinc chloride may also be used.[2]

For the synthesis of more complex ethers the method of catalytic dehydration of the corresponding alcohols is in general unsuitable. It is found that at the temperatures necessary to effect dehydration to ether, the complete dehydration to hydrocarbon also occurs to a marked degree. Thus, even with propyl alcohol, a considerable amount of propylene is formed simultaneously with the ether, the yield of which, therefore, is correspondingly reduced. The predominance of hydrocarbon formation is still more marked in the case of secondary and tertiary alcohols.

Mixed ethers may be obtained by using two alcohols with sulphuric acid as catalyst. In this manner, a mixture of the two dialkyl ethers and the mixed ether are obtained. Methyl-ethyl, ethyl-propyl, and ethyl-isoamyl ethers have been thus prepared.[3]

In the vapour phase the elimination of water produces, mainly, the corresponding hydrocarbon. Only with alumina at 210° has the production of ethyl ether been noted.[4] At more elevated temperatures, production of ethylene is practically quantitative. Baskerville[5] failed to get ether from alcohol using thoria as agent, even at temperatures as low as 250°. With phenols, however, in presence of thoria at 400°-500°, aromatic oxides result

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[1] Boulay, *Annalen*, 1913, **44**, 270.

[2] Masson, *ibid*, 1839, **31**, 63.

[3] See, for example, Peter, *Ber.*, 1899, **32**, 1419.

[4] See, for example, Pease and Yung, *J. Amer. Chem. Soc*, 1924, **46**, 391, 2297.

[5] *J. Amer. Chem. Soc.*, 1913, **35**, 93.

$$2C_6H_5.OH = (C_6H_5)_2O + H_2O,$$

and simultaneous dehydration of a phenol and alcohol, using thoria at a temperature of 400°, gives a mixed aliphatic aromatic ether

$$C_6H_5.OH + C_2H_5.OH \longrightarrow C_6H_5.O.C_2H_5 + H_2O$$

Hydrocarbons by dehydration of alcohols. The mineral acids are the normal agencies for the dehydration of alcohols to yield hydrocarbons, the operating temperature being higher than in the case of ether formation. Thus alcohol and sulphuric acid at 160°-170° yield ethylene. At 140° ether is the main product.

A variety of other catalytic materials has been employed to effect the dehydration of alcohols to yield hydrocarbons. A clue to the nature of suitable agencies for such operations is at hand in the well-known practice of adding sand to the sulphuric acid-alcohol mixture employed for the preparation of ethylene, in order to ensure a steady gentle evolution of the gas. Grigorieff[1] first indicated the use of alumina as a dehydrating agent for alcohols. Ipatiew[2] studied this action also and found that graphite was active, probably by reason of its content of clay. Extended investigation of such catalytic agents, principally by Sabatier and Mailhe[3] has shown that carbon, phosphorus, and a number of oxides, as well as solid dehydrating agents such as zinc chloride, basic aluminium sulphate, and anhydrous calcium sulphate, all promote the dehydration of alcohols.

Animal charcoal is, when compared with certain metallic oxides, a relatively poor dehydrating catalytic agent. It is markedly inferior even to red phosphorus, which possesses quite active catalytic influence, with, however, the disadvantage that small quantities of phosphoretted hydrogen are simultaneously produced and must be removed from the resulting gaseous products.

Sabatier and Mailhe[4] investigated the activity of oxide catalysts at temperatures in the neighbourhood of 300°-400°. It was shown that the majority of oxides promote two reactions simultaneously—one the process of dehydration, the other the process of dehydrogenation. By analysis of the gaseous products resulting from the dehydration of ethyl alcohol it was possible to show that, with certain catalysts, ethylene was exclusively produced, but that, generally, it was admixed with a certain proportion of hydrogen. The following table shows a series of oxides arranged in the order of activity as dehydrating agents, the figures referring to the percentage of ethylene in the ethylene-hydrogen mixture produced by passage of alcohol vapour over the oxide mass maintained at 340°-350°.

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[1] *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 173; *Bull. Soc. Chim.*, Paris, 1902 (iii.), **26**, 612.

[2] *Ber.*, 1901, **34**, 596; 1902, **35**, 1047; 1903, **36**, 1990.

[3] *Ann. Chim. Phys.*, 1910 (viii.), **20**, 289.

[4] *Loc. cit.*

	Per cent.	
ThO_2	100	Dehydrating agents.
Al_2O_3	98.5	
W_2O_3	98.5	
Cr_2O_3	91	Mixed dehydration and dehydrogenation.
SiO_2	84	
TiO_2	63	
BeO	45	
ZrO_2	45	
U_3O_8	24	
Mo_2O_5	23	
Fe_2O_3	14	
V_2O_3	9	
ZnO	5	
MnO_2	0	Dehydrogenation agents.
SnO	0	
CdO	0	
Mn_3O_4	0	
MgO	0	
Cu	0	
Ni	0	

The figures indicate that thoria is exclusively a dehydrating agent under the conditions named, whilst alumina and the blue oxide of tungsten are practically quantitative in this respect. With the remainder, however, the dehydrogenation process more and more predominates, until finally with oxides like SnO and CdO the dehydrating action is entirely suppressed.

In regard to the three effective agents, Sabatier reached the following conclusions. Thoria is the most robust. Its activity decreases but slowly, and may readily be restored by ignition to redness. The blue oxide of tungsten is prepared *in situ* by reduction of tungsten oxide, and may be rejuvenated by reoxidation and subsequent reduction. Alumina is very sensitive as a dehydrating agent to the physical state of the catalyst. An active form is prepared by dehydration of the washed precipitated hydroxide (obtained by the decomposition of sodium aluminate with sulphuric acid or from the nitrate by precipitation) at a temperature of 300°. Ignition at higher temperatures renders the catalyst considerably less active. On the contrary, the active material prepared at 300° is very sensitive to accumulations of decomposition products in the catalyst mass, and its reactivity rapidly diminishes on this account. According to Milligan [1] bauxite has marked catalytic activity, varying widely with the sample.

The relative efficiencies of such oxide catalysts have also been investigated by Adkins and his co-workers.[2] They conclude that in the comparison of chemically identical substances for a given reaction, for example the dehydration process under consideration, the method of preparation may be more important than the chemical composition of the catalyst Their work shows also that the state of a catalyst, as determined by preparation and pre-treatment, governs not only its absolute activity, but also its relative activity towards two or more alternative reactions Furthermore, they indicate that it is easier to duplicate relative activities than absolute activities in different catalyst preparations by the same method As illustrative of the selectivity secured by method of preparation of the catalyst, Bischoff and Adkins[1] have recently shown that with seven different titania catalysts, prepared from butyl titanate, titanic acid, ethyl titanate, methyl titanate, titanous chloride, sodium titanate, Demarcay's oxytitanates, and isopropyl titanate, a progressive decrease in the ratio $C_2H_4/C_2H_6+H_2$ is obtained in the dehydration of ethyl alcohol A fivefold variation in this ratio is secured with these seven catalysts

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[1] Sabatier-Reid (Van Nostrand & Co., 1922), p. 253.

[2] *J. Amer. Chem. Soc.*, 1922, **44**, 385, 2175, 1923, **45**, 809, 1924, **46**, 130, 1925, **47**, 807.

The ethane produced in this reaction is ascribed by Bischoff and Adkins to a simultaneous autoxidation and reduction.

$$2CH_3CH_2OH = CH_3 . CH_3 + CH_3CHO + H_2O,$$

one molecule of alcohol being oxidised to alcohol and the other reduced to the hydrocarbon There is no evidence that the ethane is formed by interaction of ethylene from the dehydration process with hydrogen from the dehydrogenation process Engelder[2] actually tried this without success and concluded, accordingly, that the 'nascent" hydrogen produced caused the hydrogenation of the ethylene Bischoff and Adkins's view is a possible alternative

Considerable attention has been given to the mechanism of ethylene production from vaporised alcohol in contact with dehydration catalysts[3] Ipatiew concluded that the reaction occurred in two steps Senderens believes that the formation of ether and ethylene are two independent reactions, but Pease and Yung do not think that his early evidence was decisive Adkins and Nissen pointed out that, in their studies a given alumina catalyst causes the formation of the same amount of ethylene from ethyl ether that it does from ethyl alcohol, although there is twice as much water formed from the alcohol as there is from the ether. Pease and Yung showed, as a complicating factor, that ether may decompose to give one molecule of alcohol and one of ethylene These latter authors conclude that the reaction to yield ethylene occurs in steps and that it is not necessary to assume direct dehydration to ethylene, although this is a possible mechanism From a study of the rate of dehydration of alcohol and ether on titania, Bischoff and Adkins show that ether is only one-half as reactive at 430° as alcohol is at a temperature of 400° They conclude from this that ethyl ether is not an intermediate stage in the production of ethylene

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[1] *J Amer Chem Soc*, 1925, **47**, 814

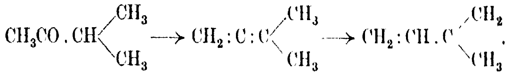
[2] *J Phys Chem*, 1917, **21**, 676

[3] Ipatiew, *Ber*, 1904, **37**, 2986, Senderens, *Bull Soc Chim*, 1908, **4**, 824, Adkins and Nissen, *J. Amer. Chem Soc*, 1924, **46**, 130, Pease and Yung, *ibid*, 1924, **46**, 390, Bischoff and Adkins, *ibid*, 1925, **47**, 814

Dehydration of aldehydes and ketones.—As is disclosed by the patent literature, the preparation of compounds containing conjugated double bonds by dehydration of aldehydes is a matter of considerable importance in view of the possible condensation of these reactive products to terpenes and rubbers. Aluminium silicate at 500°-600° is stated to be an effective dehydrating agent for this purpose. Thus U.S.P. 1033327/1912 claims the use of this material for the dehydration of butyraldehyde and valeraldehyde, *e.g.*

$$CH_3 . CH_2 . CH_2 . CHO \longrightarrow CH_2 : CH . CH : CH_2.$$

Methyl isopropyl ketone when passed over kaolin above 400° gives isoprene,[1] probably via 3-methyl-butadiene:



$$CH_3CO . CH\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right. \longrightarrow CH_2 : C : C\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right. \longrightarrow CH_2 : CH . C\left\langle\begin{matrix}CH_2\\CH_3\end{matrix}\right. .$$

Dehydration of amides yielding nitriles.—Amides, either in the liquid state or, better still, in the vapour phase, undergo dehydration, in the presence of a variety of catalysts, to give the corresponding nitrile.[2] Thus, from acetamide, acetonitrile can readily be obtained:

$$CH_3CONH_2 = CH_3CN + H_2O,$$

with alumina, pumice, and sand as catalysts. There is some evidence in the data given by the authors cited that equilibrium is attained in the liquid state at about 68 per cent nitrile formation at a temperature of 250°-260°. In the vapour phase, at 420°, a 90 per cent conversion was attained. The aldoximes, which are isomeric with the amides, yield nitriles by similar treatment.

Van Epps and Reid produced the amide from acid and ammonia and dehydrated the amide as formed in a single operation,[3] alumina being a convenient catalyst operating at a temperature of 500° C. An 85 per cent yield of nitrile was thus obtained from acetic acid.

Adkins and Nissen[4] showed that the formation of nitriles from amides is not affected by modifications in the preparation of the catalyst, in sharp contrast to the reactions of alcohols already discussed. They ascribe this to the lack of influence of spatial relationships of the catalyst material. It may be, however, that the real reason is that practically the whole of an alumina surface is active in this reaction and only a small part of the surface in the alcohol case. Possibly some clue to a decision in this matter could be reached by a study of the relative poisoning of the catalysts in the two reactions.

Dehydration of hydroxy-acids yielding lactones.—The elimination of water from hydroxy-acids with formation of lactones is a dehydration process catalytically accelerated by acids The reaction occurring, which may be generalised as follows

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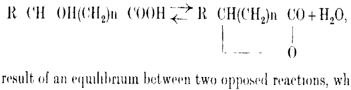
[1] Earle and Kyriakides, U.S.P. 1106290; *J. Soc. Chem. Ind.*, 1914, **33**, 942.

[2] Boehner and Andrews, *J. Amer. Chem. Soc.*, 1916, **38**, 2503; Boehner and Ward, *ibid.*, 1916, **38**, 2505.

[3] *J. Amer. Chem. Soc.*, 1916, **38**, 2128.

[4] *J. Amer. Chem. Soc.*, 1924, **46**, 130.



$$R\ CH\ OH(CH_2)n\ COOH \rightleftarrows R\ CH(CH_2)n\ CO + H_2O,$$

is the result of an equilibrium between two opposed reactions, which, in presence of acids in dilute aqueous solution, where the concentration of water may be regarded as constant, are unimolecular and are both catalytically promoted by addition of acids The reaction velocity in such a process is given by the equation

$$\frac{dx}{dt} = k_1(a - x) - k_2x,$$

where a is the initial concentration of hydroxy-acid, x the amount transformed at time t, and k_1 and k_2 the reaction constants of lactone formation and the reverse hydrolysis respectively in presence of the added acid

If the equilibrium constant of the reaction be K, then

$$K = \frac{k_1}{k_2},$$

and consequently

$$\frac{dx}{dt} = k_2K(a - x) - k_2x$$

and this expression, on integration, yields, as was shown by P Henry,[1] the equation

$$k_1 + k_2 = \frac{1}{t}\log\frac{Ka}{Ka - (K + 1)x}$$

The equation gives values for the sum of the two reactions in terms of the equilibrium constant and the quantities of acid and lactone present at the times t_0 and t It was tested experimentally by Henry in the case of hydroxybutyric acid good reaction constants for $(k_1 + k_2)$ being found with the aid of the experimentally determined equilibrium constant $K = 2{\cdot}68$ In the conversion of oxyvaleric acid to valerolactone it was found that the equilibrium concentration of lactone is more than 92 per cent of the original concentration of hydroxy-acid, so that the influence of the reverse reaction on the velocity of lactone formation was small, and the process occurring could be treated as a simple unimolecular reaction with the velocity equation

$$k_1 = \frac{1}{t}\log\frac{a}{a - x},$$

to which, obviously, also, the above equation for the two opposing reactions reduces when $K=\frac{k_1}{k_2}$ becomes large in comparison with the other magnitudes.

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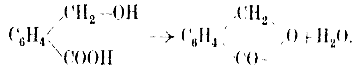
[1] *Zeitsch physikal Chem*, 1892, **10**, 98

Studied thus as a unimolecular reaction, it was shown by Henry that the conversion of oxyvaleric acid to valero-lactone was catalytically accelerated by acids in proportion to the concentration of the hydrogen ions. A more exact study of this reaction[1] in presence of varying concentrations of catalysing acid with and without the addition of neutral salts having a common ion, has shown that the proportionality to hydrogen-ion concentration is not, however, an exact one, but that the deviations are analogous in every way to those already observed and noted in the case of catalytic hydrolysis and synthesis of esters, and that, therefore, the same explanations of mechanism of the catalytic activity may also be employed in this case.

Since hydrogen ions are catalytically active in promoting lactone formation, it is obvious that the hydrogen ions formed by solution of the acid itself in water will accelerate the reaction - another example of auto-catalysis. Furthermore, since in the progress of auto-catalytic action the concentration of hydroxy-acid is progressively diminished with formation of lactone, it is obvious, also, that the auto catalytic activity, and consequently the rate of reaction, will diminish. The reaction thus affords an interesting example of auto retardation. The influence of these two factors of auto-catalysis and auto retardation on the velocity of lactone formation in aqueous solution was specially investigated and mathematically formulated by Collan[2] in a study of the conversion of carboxybenzyl alcohol to the cyclic lactone, phthalide :



$$C_6H_4\left<\begin{array}{l}CH_2-OH\\COOH\end{array}\right. \rightarrow C_6H_4\left<\begin{array}{l}CH_2\\CO\end{array}\right>O+H_2O.$$

The reaction has been studied in further detail by Kailan and Neumann,[3] who have shown that with hydrochloric-acid concentrations up to one-fifth normal the velocity is almost exactly proportional to the acid concentration, and, therefore, rises much more rapidly than the hydrogen-ion concentration. At higher concentrations of catalysing acid the increase in velocity is more rapid than that of the hydrogen-ion concentration but less rapid than that of the molar concentration. They attribute the catalytic activity, therefore, to the hydrogen ions solely and ascribe the deviations from strict proportionality to a salt effect of the extra acid similar to, but less than, that exerted by neutral salts.

The reaction is one which is adapted to study in solvents other than water. Kailan and Neumann have studied the reaction velocity in alcohol and alcohol-water mixtures. They find that the formation of lactone proceeds much faster in 99 per cent alcohol than in water, both in presence and absence of hydrochloric acid as catalyst They show also that water exerts a much more marked retarding action on the catalytic process than is found in esterification processes (p 364) With increasing additions of water to the alcohol the velocity falls below that in pure water, shows, therefore, a minimum such as is found in the decomposition of diazo esters in alcohol-water mixtures

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[1] Taylor and Close, *J. Amer. Chem. Soc.*, 1917, **39**, 422.

[2] *Zeitsch physikal. Chem.*, 1892, **10**, 100.

[3] *Ibid.*, 1920, **94**, 111 ; 1922, **101**, 63.

Taylor and Close have also studied the velocity of lactone formation in ether and in ether-water solutions, using hydroxymethyl benzoic acid[1] They found a negligible reaction velocity in dry ether which was tenth normal with respect to hydrogen chloride This result seems definitely to establish that undissociated molecules have no catalytic activity They found, however, that in ether saturated with water and also tenth normal with respect to hydrogen chloride the velocity of formation of the lactone, phthalide, was extremely rapid as compared with the velocity in aqueous hydrogen chloride or in acid solutions containing dissolved ether This result very definitely establishes the fact that the reaction velocity is not directly proportional to the acid concentration or to the hydrogen-ion concentration, since this latter is very much greater in water solution than in ethereal solutions, if measured by conductance of the solutions

The result obtained is, however, in qualitative agreement with the theory that it is the activity function of the catalyst which determines the reaction velocity For, from distribution experiments, it is known that hydrogen chloride distributes itself between ether and water in such a way that more than 99 per cent of the acid is in the aqueous layer Comparison should therefore be made of reaction velocities in the two solvents not at equal acid concentrations but at concentrations in the distribution ratio of the hydrochloric acid in the two solutions

Dehydration of fatty acids.—Attempts to eliminate water from the aliphatic acids are, with the exception of formic acid, only achieved with simultaneous evolution of carbon dioxide and rupture of the molecule, the product being ketonic or aldehydic in nature

Formic acid may be decomposed in several ways and in presence of certain catalysts with elimination of water. Thus the possibilities may be formulated by the equations

$$
\begin{aligned}
&(1)\quad \mathrm{H\,COOH} \longrightarrow \mathrm{H_2O} + \mathrm{CO},\\
&(2)\quad \mathrm{2H\,COOH} \longrightarrow \mathrm{H\ CHO} + \mathrm{CO_2} + \mathrm{H_2O},\\
&(3)\quad \mathrm{3H\,COOH} \longrightarrow \mathrm{CH_3\ OH} + \mathrm{CO_2} + \mathrm{H_2O},
\end{aligned}
$$

whilst dehydrogenation may simultaneously occur in effecting one or other dehydration process, according to the reaction

$$\mathrm{H\,COOH} \longrightarrow \mathrm{CO_2} + \mathrm{H_2}$$

The primary process of dehydration to yield carbon monoxide and water is that normally occurring on treatment of formic acid with strong dehydrating agents such as sulphuric acid or anhydrous oxalic acid. The reversibility of this process has long been known, and is the basis of modern technical practice for the synthesis of formic acid. Actually, use is made of a base such as soda, the product being, therefore, a formate. The equilibrium occurring in the process is calculable, according to the Nernst heat theorem, from the thermal constants of the reacting substances.

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[1] Close, Dissertation, Princeton, 1922

Thus, for the gas reaction, according to Pollitzer,[1] the heat of reaction:

$$CO + H_2O = H.COOH + 9300 \text{ cals.}$$

can be obtained from the heats of combustion, and amounts to 9300 cals. for gaseous formic acid. Utilising the Nernst approximation formula and values for the "chemical constant":

$$C_{H_2O} = 3{\cdot}6, \quad C_{CO} = 3{\cdot}5, \quad C_{H\,COOH} = 3{\cdot}5,$$

there follows for the equilibrium equation:

$$\log \frac{CO \times H_2O}{H\,.\,COOH} = -\frac{9300}{4{\cdot}571\,T} + 1{\cdot}75 \log T + 3{\cdot}8,$$

which gives the following values for K:

$T^\circ =$	300°	500°	1000° abs.
$K =$	20	3×10^4	10^7.

According to this result, formic acid decomposes practically quantitatively to carbon monoxide and water when but slightly heated. On the other hand, the equilibrium concentration of the acid at the ordinary temperature should be demonstrable, especially if increased by application of pressure to the system

In the researches of Branch[2] the equilibria prevailing at 156° and 218° with gas-liquid phases were actually determined. It was shown that the decomposition was reversible and that mineral acids, especially hydrochloric acid, acted as catalysts

The equilibrium constants given by the measurements represent that of the reaction:

$$H\,.\,COOH_{1M} = H_2O_{liq} + CO,$$

the values of K being 89·9 and 310 at 156° and 218°, when the CO concentration was expressed in atmospheres pressure, that of the formic acid in mols. per litre, the water as the ratio of its concentration to that in pure water.

It was shown that with ½ N-hydrochloric acid as catalyst no appreciable side reactions occurred, the gas formed being pure carbon monoxide.

Sabatier and Mailhe[3] have shown that in the vapour phase various oxide catalysts act similarly Thus oxide of titanium at 170°-320° gives carbon monoxide in a marked degree of purity, and this is true also of blue oxide of tungsten at 270° Alumina, silica, zirconia, and uranous oxide give mainly carbon monoxide, but a certain proportion of formaldehyde is simultaneously formed according to reaction (2) With uranous oxide, this latter reaction is almost as important as the simple dehydration process With thoria the change commences at 250°-375°, with production of all the products of dehydration The proportions of each progressively alter with rise in temperature of decomposition At 250° the gaseous product contains 73 per cent CO, 15 per cent CO_2, and 10 per cent H_2, together with a small quantity of liquid formaldehyde At 320° there is about 45 per cent CO in the gas and considerable quantities of the condensation product of formaldehyde and methyl alcohol This latter increases in percentage with increase in temperature, due to the further decomposition of formaldehyde to carbon monoxide and hydrogen As a result of a study of the decomposition of the formates, Hofmann and Schibsted found[1] that the yield of formaldehyde was greatest from zinc and stannous formates The corresponding oxides would be expected to be most efficient in the catalytic decomposition of formic acid to yield formaldehyde

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[1] *Berechnung chemischer Aff. Ahrens Sammlung*, 1912, p. 443.

[2] *J. Amer. Chem. Soc.*, 1915, **37**, 2316.

[3] *Compt. rend.*, 1911, **152**, 1212.

MIXED DEHYDRATION

Homogeneous esterification. The elimination of the elements of water from an alcohol and an acid jointly gives rise to the formation of compounds known as esters, and the process itself is termed esterification The reaction occurring may be generalised in the case of monobasic carboxylic acids by the equation

$$R\ COOH + R_1\ OH = R\ COOR_1 + H_2O,$$

and, in a similar manner, reactions between polybasic carboxylic and other acids may be generalised

The reaction occurring, as was shown in the classical studies of Berthelot and Paen de St Gilles as early as 1862, is a beautiful example of the reversible or balanced action It is definable as to the equilibrium position by means of the Guldberg-Waage law of mass action formulated in 1867, and therefore subsequent to the actual experimental proof furnished by the studies on esterification The researches of Berthelot and St Gilles demonstrated that with equivalent initial concentrations of acetic acid and ethyl alcohol, for example, there was present at equilibrium one-third of the original concentrations of acid and alcohol, and two-thirds of ester and water According to the mass-action law, therefore,

$$K = \frac{C_{\text{acid}} C_{\text{alcohol}}}{C_{\text{ester}} C_{\text{water}}} = \frac{0{\cdot}33 \times 0\ 33}{0{\cdot}66 \times 0\ 66} = \frac{1}{4}.$$

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[1] *Ber*, 1918, 51, 1398

It was further demonstrated that with varying proportions of alcohol this mass-action constant was maintained, and that, therefore, in presence of excess of alcohol a high percentage of acid could be transformed to ester.

It was pointed out in the preceding chapter that the reverse action in this process, the hydrolysis of an ester, is catalytically accelerated by the addition or presence of numerous substances, and chief among such accelerating agents were acids. As is therefore to be expected, acids are also catalytic agents in the production of esters and have been consistently so used in preparative organic chemistry. Since acids behave as catalytic agents, it is obvious that the reaction between an alcohol and an acid is an auto-catalytic process, the acid undergoing esterification being itself a catalyst of the reaction. In general, however, and especially in the esterification of weak acids, as, for example, acetic acid, addition of a strong acid catalytic agent is general. Formerly, the principal acid catalyst was sulphuric acid, and it is still occasionally made use of as a convenient agent. Frequently, however, owing to its strong dehydrating and charring action, its use is impossible. In agreement with the observations made in the section on hydrolysis, the strong acid, hydrochloric acid, is, however, the better agent, and use of this acid is the basis of the modern method of esterification as worked out by Emil Fischer and Speier.[1] The method employed by them consists in heating the acid to be esterified with an excess of alcohol containing about 3 per cent of dry hydrogen chloride dissolved in it as catalytic agent. After a period of time, dependent on several factors to be more fully discussed later, equilibrium is attained, and the ester may be obtained therefrom in several ways. By raising the temperature to the boiling point of the mixture, the velocity of reaction is greatly accelerated. An earlier method employed by v. Meyer and Sudborough[2] was operated at the ordinary temperature, compensation for the relative slowness of the reaction being effected by using saturated solutions of hydrogen chloride in the alcohol.

The more recent researches of Senderens and Aboulenc[3] demonstrate, however, that sulphuric acid can operate in a similar manner to hydrochloric acid. It was shown that on distillation of equimolecular proportions of acetic acid and ethyl alcohol 17·8 per cent of the theoretical amount of ethyl acetate was formed. With 1 per cent of sulphuric acid by volume, however, the yield is 86·5 per cent of theory. The general applicability of this method was demonstrated in later papers.[4] Anhydrous aluminium sulphate and potassium hydrogen sulphate were also shown to be effective catalytic agents, 82 per cent yields being obtained. Anhydrous sodium sulphate was without action, however, showing that the activity is not entirely due to the dehydrating action. This latter was emphasised by Kurtenacker and Habermann,[1] who also studied various other salts. A German patent[2] combines both dehydrating and catalytic activity in a proposal to produce ester quantitatively from alcohol and acid by boiling the components in presence of anhydrous calcium chloride and a mineral acid

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[1] *Ber.*, 1895, **28**, 3252.

[2] *Ibid.*, 1894, **27**, 510.

[3] *Compt. rend.*, 1911, **152**, 1671.

[4] For example, *Compt. rend.*, 1913, **156**, 1620.

The velocity of esterification is sufficiently slow for convenient study, the progress of reaction being readily determined by the diminishing acid content of the system, due to the production of ester As in the case of hydrolysis, therefore, the process of esterification has been the object of considerable study with a view to the elucidation of the theoretical aspects of the catalytic process

The relationship between chemical constitution of acid and alcohol and the esterification process has occasioned considerable research The work of Menschutkin[3] on the auto-catalytic esterification of fatty acids demonstrated that the velocity of esterification diminished with increasing complexity of the acid and of the alcohol, it was more rapid, however, in the case of primary alcohols than with secondary or tertiary alcohols Side chains, negative substituents, and unsaturated linkages in a primary alcohol also caused diminution of esterification velocity These latter conclusions were supported by the subsequent determinations of Michael and Wohlgast[4] on the esterification of trichloroacetic acid by various alcohols Exceptions to Menschutkin's observations are, however, noted by Lichty[5] in the case of chlorinated fatty acids, introduction of a chlorine grouping accelerating the velocity of esterification over that of the simple acid

Parallel experiments on constitutive influence in the case of esterification in presence of hydrogen chloride as catalyst were first undertaken by v Meyer, alone and in conjunction with Sudborough[6] It was shown, for example, that diortho-substituted benzoic acids were very resistant to esterification, the degree of inhibition being governed to a certain degree, however, by the nature of the substituent Thus, the influence of hydroxyl and methyl substitution was not so marked as that of nitro-, halide, and carboxylic radicals Substitution in other than the ortho-position had comparatively little inhibitory effect on the Fischer-Speier esterification method. The literature of this type of investigation has been multiplied enormously by the organic chemist with a view to the determination of constitutive influence, more especially as to the operation of steric hindrances[7]

The researches of Goldschmidt and his pupils into the problem of esterification have been carried out with a somewhat different object, employing dilute alcoholic solutions of the acid to be esterified and using hydrogen chloride and other acids as catalyst. In such circumstances the concentration of alcohol can be regarded as constant and the reaction velocity as interpretable by means of the unimolecular equation

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[1] *J pr Chem*, 1911 (ii), **83** 541

[2] D R P 232818

[3] *J pr Chem*, 1881 (ii), **24**, 49, 1882 (ii), **25**, 103 *Ber*, 1897 **30**, 2783

[4] *Ber*, 1909, **42**, 3157

[5] *Amer Chem J*, 1895, **17**, 27, 1896 **18**, 590

[6] *Ber*, 1894, **27**, 510, 1580, 3146 1895, **28**, 182, 1254

[7] See especially Sudborough and his co workers, *J Chem Soc*, 1898, **73**, 81, 1905, **87**, 1840, 1907, **91**, 1033, 1909 **95**, 315, 975, Wegscheider, *Monatsch*, 1895, **16**, 75, 1897, **18**, 418, 629, 1899, **20**, 685, 1900, **21**, 621, 638, 787, 1902, **23**, 317, 357, 369, 393, 405, 1093, 1903, **24**, 413, 915, 1905, **26**, 1039, 1906, **27**, 487, 777, 1907, **28**, 819, 1908, **29**, 525, 531, 535 541 557 1910 **31** 1253

$$K = \frac{1}{t} \log \frac{a}{a - x}.$$

Operating in this manner, it was shown that, as a rough approximation, the reaction constant varied proportionately to the hydrogen-ion concentration, and that the activity of different acid catalytic agents was in direct relation to the strength of the acid as determined by the hydrogen-ion concentration from conductivity data in alcoholic solution. Thus, in order of diminishing catalytic activity, came hydrochloric, picric, trichloroacetic, trinitrobenzoic, trichlorobutyric, and dichloroacetic acids. Goldschmidt further showed that the ratio of the velocities of esterification of an organic acid with two different catalysing acids was constant and independent of the particular acid esterified in a given alcoholic solution. Thus, as the following table reveals, the ratio of the velocities and esterification, using hydrochloric and picric acids, averaged 13·5 with acetic, propionic, *n*-butyric, and phenyl acetic acid.

Acid.	k_a. N/10-HCl	k_b N/10-Picric Acid	k_a/k_b
Acetic . . .	2·179	0·162	13·5
Propionic . . .	1·544	0·115	13·4
n-Butyric . . .	0·764	0·0582	13·1
Phenyl acetic .	0·902	0·0655	13·8

With hydrochloric and sulphosalicylic acids as catalytic agents the ratio was similarly constant.

Observation of the retardation of reaction velocity due to the influence of small quantities of water produced during the process of esterification or added to the reaction medium[1] led Goldschmidt[2] to the hypothesis that the active catalytic agent of the esterification process was an alcoholate,

$$(C_2H_5 . OH . \dot{H}),$$

of the hydrogen ion of the catalysing acid. This alcoholate was regarded as interacting with the acid to be esterified, yielding the ester product. The retarding action of water was ascribed to reduction of the concentration of the active alcohol by hydrolysis to yield a non-active ion hydrate:

$$(C_2H_5 . OH . \dot{H}) + H_2O \rightleftarrows C_2H_5 . OH + (H . OH . \dot{H}).$$

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[1] Goldschmidt, *Ber.*, 1895, **28**, 3218; with Sunde, *ibid.*, 1906, **39**, 711; Kailan, *Monatsh.*, 1907, **28**, 115, 559 *et seq.*; 1908, **29**, 799.

[2] *Zeitsch. Elektrochem.*, 1906, **12**, 432.

Thus if ζ = the equilibrium concentration of the ion alcoholate,

n = the initial concentration of added water,

x = the concentration of acid esterified and therefore of water formed in the reaction,

r = the equilibrium or hydrolytic constant of the above hydrolysis,

y = the equilibrium constant of ion hydrate,

there follow, according to the mass-action law,

$$C_{C_2H_5\cdot OH\cdot\dot{H}} \times C_{H_2O} = r\, C_{C_2H_5\cdot OH} \times C_{H_2O\cdot\dot{H}}$$

or

$$\zeta(n + x - y) = ry \tag{1}$$

In presence of excess of alcohol, which may therefore be regarded as constant a simplified treatment of the problem may be obtained if assumption be made that y, the concentration of ion hydrate, may be neglected in comparison with $(n + x)$, the total quantity of water present In such cases Equation (1) becomes

$$\zeta(n + x) = r\,y \quad \text{or} \quad y = \frac{\zeta(n + x)}{r}, \tag{2}$$

the term r including the alcohol concentration term, assumed constant

If ζ_0 represent the ion-alcoholate concentration in total absence of water, it follows that

$$\zeta_0 = \zeta + y \tag{3}$$

ζ_0 may be expressed, by application of the mass action law to the equation

$$C_2H_5\cdot OH + \dot{H} \rightleftarrows (C_2H_5\cdot OH\cdot\dot{H}),$$

in terms of c, the $\dot{H}$ ion concentration in absolute alcohol, the concentration of alcohol in mols per litre (b), and ϕ the equilibrium constant of this reaction

Thus $$\phi\cdot c\cdot b = \zeta_0$$

Substituting this value in (3) we obtain the values of ζ or y in terms of these magnitudes, viz

$$\zeta = \phi bc - y,$$
$$y = \phi bc - \zeta,$$

whence from Equation (2)

$$\zeta = \frac{\phi bc\, r}{n + x + r} \tag{4}$$

Now the velocity with which esterification occurs is proportional at any moment to the amount of unesterified acid and to the concentration of the catalyst, ζ That is,

$$\frac{dx}{dt} = k(a - x)\zeta,$$

where a is the original concentration of the acid undergoing esterification. Substituting the value for ζ obtained in (4), there results

$$\frac{dx}{dt}=k(a-x)\frac{\phi bc\,.\,r}{n+x+r},$$

and this on integration gives the result

$$k\,.\,c\,.\,t\,.=n+r+a\log\frac{a}{a-x}-x. \qquad . \qquad . \qquad . \quad (5)$$

By determining two values of x at times t_1 and t_2 we obtain thereby, with Equation (5), two equations from which the value of r may be calculated. In this way Goldschmidt calculated a value for the hydrolytic constant $r=0{\cdot}15$ at 25° for hydrochloric and sulphosalicylic acids, the value varying but little with a whole series of different acids esterified in ethyl alcohol solution. At 0° the value of r becomes 0·095.

The falling constant, K, obtained by application of the ordinary unimolecular equation and caused by the inhibiting influence of the water formed in the reaction, was to a marked degree corrected for by use of Equation (5). Application of a still more exact, but also more complicated, formula obtained without neglecting the concentration of the ion hydrate y, as compared with $n+x$, gave even better concordance in the reaction constants.

The problem of retardation by traces of water has also been the subject of investigation by Lapworth and his co-workers. Lapworth and Fitzgerald[1] emphasised the point of view that the water acted by reducing the concentration of the free hydrogen ions present in the alcoholic solution by a simple process of hydration. Contrary to the Goldschmidt point of view, the free hydrogen ion and not the alcoholate is assumed active; the ion hydrate, as with Goldschmidt, is regarded as inactive. In a subsequent paper[2] Lapworth directed attention to a number of reactions in which the anti-catalytic effect of water was marked, and proceeded to a mathematical development of the view put forward in the earlier paper. The addition of water to a dilute solution of hydrogen chloride in alcohol was regarded as the addition of a relatively strong base to a solution of an acid in a weak base. On this assumption, and making allowance for the removal of the catalytically active hydrogen ions by both water and alcohol as ion hydrate and ion alcoholate, Lapworth deduced for the velocity of esterification the equation

$$\frac{-du}{dt}=AK_2pxM'\frac{M}{\frac{K_2}{K'_2}M'+M},$$

where u is the active mass of the carboxylic acid.

p = a constant dependent on the nature of this acid,

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[1] *J. Chem. Soc.*, 1908, **93**, 2167.

[2] *J. Chem. Soc.*, 1908, **93**, 2187.

M and K_2 refer to the active mass of water and equilibrium constant of the ion-ion hydrate equilibrium,

M' and K'_2 the corresponding magnitudes for alcohol,

x is the measured degree of dissociation, and A the total mass of the catalysing acid

This is in accordance with the observations of Goldschmidt and Udby and with the equation previously deduced (p 369)

$$\frac{dx}{dt} = k(a-x)\frac{\phi bc\,r}{n+x+r},$$

as will be evident from the following comparison of symbols

(G)	$k\phi$	b	r	c	$a-x$	$n+x$
(L)	$\frac{pK'_2}{M'}$	M'	$\frac{K_2}{K'_2}M'$	Ax	a	M

The interpretations of the two equations, however, are by no means identical, for whereas Goldschmidt assumes that the ion alcoholate is the active catalytic agent in order to derive his equation, Lapworth assumes that the velocity of esterification is at any time proportional to the active masses of the carboxylic acid, the alcohol, and the free hydrogen ions

To test further the idea of the availability or salt-forming power of an acid in various solvents on addition of a base relatively stronger than the solvent, preliminary tintometric determinations were made in alcoholic solutions of hydrogen chloride and in benzene and carbon tetrachloride solutions of trichloroacetic acid, using various bases and aminoazobenzene as indicator Concordant values were obtained for the relative basic affinities in decreasing order of a series of weak bases, the order being carbamide, water, ether, ethyl alcohol, acetone, ethyl acetate, and methyl alcohol

A later publication[1] dealt more particularly with the "availability" of hydrogen chloride in alcoholic solution and the influence of water thereon In this publication the availability of the acid is defined as a function proportional to its capacity for forming complex hydrions with any mono-acid base, which, mathematically expressed, becomes

$$P = \frac{\xi}{kB},$$

where P is the availability, ξ the concentration of complex ions, and B the concentration of free base, k the constant for the base used By tintometric and esterification experiments the availability of a very dilute solution of hydrogen chloride in moist alcohol was shown to be nearly an inverse linear function of the amount of water present for quantities of the latter not exceeding a concentration of 0·5 mol per litre. The availability in this range could be represented by an expression

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[1] Lapworth and Partington, *J Chem Soc*, 1910 **97**, 19

$$\frac{c\,k}{r+w},$$

where c = concentration of hydrogen chloride,
k = a constant,
w = concentration of water,
r = the water equivalent of the alcohol present, constant, as was shown by Goldschmidt and Udby, for a given alcohol, but within experimental error the same by measurements either of esterification or by determination of the salt formed with a weak mono-acid base.

Interesting in regard to this latter conclusion of Lapworth and Partington is the conclusion reached by Bredig, Millar, and Braune that r (the water equivalent or basic water value of Lapworth and Partington; the hydrolytic constant of Goldschmidt) was numerically the same, in diazoacetic-ester decomposition in aqueous alcoholic solution, as in esterification measurements. This identity naturally suggests a common cause in each case, and, moreover, is of importance in a decision of the relative merits of the two points of view. For, as was pointed out in the preceding chapter in reference to diazo ester decomposition, the Goldschmidt assumption of non-activity of the ion hydrate leaves only the hydrogen ion as the catalytic agent for the decomposition of diazo ester in *aqueous* solution, and yet, in esterification, Goldschmidt's theory assumes both free ion and ion hydrate to be inactive, but the ion alcoholate, however, to be active. In Lapworth's view, the free ion is the active agent, and is determined by the availability of the acid. Obviously, therefore, Lapworth's theory is applicable without modification to all the various acid catalytic processes here considered, whilst Goldschmidt's view requires adjustment to meet particular cases.

Lapworth and Jones[1] have extended the investigations to studies of the influence of temperature on the basic water value, r, of the theory, and also to measurements of vapour pressures of hydrogen chloride in moist alcoholic solutions, in order to obtain further evidence on the point of view put forward. It was shown both by the tintometric and by the esterification method that the value of r steadily increased with temperature from a value of 50×10^{-3} at 0° to 97×10^{-3} at 25°, in quantitative agreement with the results of Goldschmidt and Udby, who, however, employed a different concentration of catalyst, which affects the absolute values obtained very considerably.

The determination of the partial vapour pressure of hydrogen chloride in alcohol in presence and in absence of water vapour served to connect the behaviour of water in the reactions previously discussed with its influence on the more directly measurable properties of solution.

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[1] *J. Chem. Soc.*, 1911, **99**, 917 *et seq.*

It was shown that the partial pressures of the hydrogen chloride are reduced very considerably by the presence of small quantities of water, as is evident from the graphical representation in Fig 18, the relative depression increasing, moreover, as the concentration of acid diminishes

The reduction caused by water on the electromotive force of the hydrogen electrode in alcoholic hydrogen chloride, investigated in the same laboratories,[1] has also been used as evidence of the point of view here set forth in explanation of the anti-catalytic effect of water in esterification processes

The influence of additions of neutral salts possessing an anion in common with that of the catalysing acid was next investigated by Goldschmidt and led to further remarkable conclusions It was shown, for example, that addition of chlorides was without influence on the velocity of esterification, using hydrochloric acid as catalyst[2] With weaker acids, addition of neutral salts repressed the velocity of esterification The retardation was, however, by no means proportional to the hydrogen-ion concentration, as calculated by application of the mass-action law to the electrolytic dissociation of the acid in presence of a salt having a common ion Instead, it was shown that addition of excess of salt repressed the velocity of reaction to a definite lower limit and no further Goldschmidt associated these observations with the conclusion that the undissociated molecules of catalyst are also active, and calculated out his experimental results in accordance with

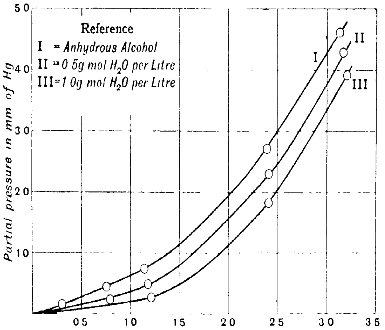

Fig 18

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[1] See Hardman and Lapworth, *J. Chem Soc.*, 1912, **101**, 2240

[2] Goldschmidt, *Zeitsch Elektrochem*, 1909, **15**, 4

this view.[1] The relation between the catalytic activity of the undissociated molecule and the strength of the acid was pointed out by Snethlage,[2] who showed from Goldschmidt's figures that the stronger the acid the greater the catalytic activity of the undissociated molecule, pointing out further that the ratio of activity of undissociated acid catalyst to that of hydrogen ion should be independent of the acid esterified. Goldschmidt and Thuessen demurred to this view as a result of investigations with methyl alcohol as solvent.[3] A recalculation of the results by Snethlage,[4] however, justifies the original assumptions. It is there also pointed out that the constancy of the reaction velocity with hydrochloric acid as catalyst in presence of chlorides is to be explained by the hypothesis that in alcoholic solution the activity of the undissociated hydrochloric acid is equal to that of the hydrogen ion, a view in agreement with the observation that the relative activity of undissociated acid to hydrogen ion increases with increasing strength of acid. The problem of the catalyst in esterification processes must, however, be considered along with the conclusions from other lines of work. There, the tendency is away from the assumption of an activity of the undissociated molecule and towards a kinetic or thermodynamic treatment of the hydrogen ion as the catalytic agent.

The complexity of the esterification process is manifest from these researches. It is evident that the operation of a number of equilibria are determining factors in the velocity with which esterification occurs. These include the actual electrolytic dissociations of the catalyst and esterified acid, the equilibria between the ions, the undissociated molecules, and the alcohol solvent, as well as the disturbing equilibria brought about by the intervention in the reaction of the water produced in the esterification process. In addition, also, the possibility of termolecular complexes in the case of the non-auto-catalytic reactions cannot be excluded. The direct or auto-catalytic esterification process has been regarded by most workers as differing in detail from the catalytic process, and it may be in the possibilities and stability of complex formations, as much as in the factors of acid strength, that the differences lie. A deeper study of this subject from such a point of view would doubtless show that the differences observed are reconcilable to the general underlying principles which have been put forward.

Esterification in the gaseous phase.—Esterification in the gaseous phase in presence of oxides as catalysts has been studied by Sabatier and Mailhe.[5] When an alcohol and an acid are simply passed through a heated tube little or no reaction occurs in the sense of the equation

$$\mathrm{R.COOH + R_1.OH = R.COOR_1 + H_2O}. \quad . \quad . \quad (1)$$

If a charge of certain oxides, as, for example, TiO_2, be placed in the tube, rapid reaction with production of high concentrations of ester will result at a temperature of 280°-300°

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[1] *Zeitsch. Elektrochem.*, 1911, **17**, 684.

[2] *Ibid.*, 1912, **18**, 539.

[3] *Zeitsch. physikal. Chem.*, 1913, **81**, 30.

[4] *Ibid.*, 1913, **85**, 238.

[5] *Compt. rend.*, 1910, **150**, 823; 1911, **152**, 358, 494, 1044.

It has been shown in a preceding section (p 356) that oxides are effective catalytic agents in promoting the dehydration of alcohols with hydrocarbon formation, according to the equation

$$C_nH_m\ OH \longrightarrow C_nH_{m-1} + H_2O \qquad (2)$$

It will later be shown that the same agents are also active in promoting the decomposition of acids with elimination of water and carbon dioxide to form ketones, as generalised by the equation

$$2R\ COOH \longrightarrow CO_2 + H_2O + R\ COR \qquad (3)$$

It will therefore be obvious that in order to promote etherification according to Equation (1) due regard must be paid in the choice of catalyst to the possibility of occurrence of the reactions (2) and (3)

Thus, it might be anticipated that thoria, which is a very efficient agent in the dehydration of alcohols and also in the decomposition of fatty acids to ketones, would not be the most suitable agent for promoting esterification in the gaseous phase On the contrary, with aromatic acids, where the tendency for reaction (3) to occur is much less, thoria may be used very effectively as an esterification agent and was so utilised by Sabatier and Mailhe in the synthesis of numerous esters of benzoic and toluic acids, *e g*

$$C_6H_5\ COOH + C_2H_5\ OH \longrightarrow C_6H_5COO\ C_2H_5 + HOH$$

The ease with which this reaction proceeds points to the fact, which is confirmed by the subsequent examples, that dehydration from an acid and an alcohol jointly occurs much more readily than dehydration of an alcohol alone

For the synthesis of fatty acid esters, the choice of titania as catalyst was justified by the results It will be observed from its position in the table cited in the section on dehydration of alcohols (p 357) that titania is much less active as a dehydrating agent than thoria, and this is likewise true for its action on fatty acids At 280°-300°, however its dehydrating action on alcohol and fatty acid jointly is very effective, and thus can be used for the synthesis of the most varied fatty acid esters

The preference of esterification over dehydration in presence of suitable oxide catalysts is also indicated by the fact that good yields of ester can be obtained even with secondary alcohols Thus, at a temperature of 300°, isopropyl alcohol may be esterified without the simultaneous production of propylene, whereas with the alcohol alone, rapid dehydration sets in with production of the hydrocarbon at a temperature of 260°

With isobutyl alcohol, decomposition into butylene sets in at 255°, even in presence of the acid, but esterification occurs below this temperature in presence of titania. Tertiary butyl alcohol and isobutyric acid esterify slightly at 235° without hydrocarbon formation.

Mailhe and de Godon[1] claim that zirconia is as good an esterification agent as titania. Milligan, Chappell, and Reid[2] have studied the esterification process extensively and conclude that silica gel is a better esterification catalyst than either. They do not find that beryllia is a catalyst, contrary to the views of Hauser and Klotz.[3] The researches of Adkins and his co-workers[4] set the matter of the suitability or otherwise of a catalyst in a somewhat different light. They conclude that it is much more the form of the catalyst material rather than the particular dehydration oxide catalyst which governs the suitability for the dehydration process. They find, for example, that aluminas prepared from different starting materials, such as precipitated alumina, aluminium-mercury couples, aluminium alkoxides, show very variable behaviour in esterification activity. The same also is found to be true for titania catalysts from different sources or different methods of preparation. They ascribe this varying behaviour to a varying spatial relationship of the active centres of the catalyst surface due to varying distances of such centres a point of view developed by Langmuir[5] to account for activation of catalyst materials It would be advantageous if some definite proof of such a spatial arrangement of active centres could be brought forward. As yet the assumption is, in reality, an *ad hoc* hypothesis, accounting for known experimental facts. It may be that only a certain fraction of the oxide surface is in reality catalytically active and that this is not the plane surface but the molecules which are detached from the normal crystal lattice, in a state of unsaturation. This latter point of view is that suggested by data on the poisoning of catalysts, adsorption by catalysts, and the data of promoter action in other types of catalytic process.

Sabatier and Mailhe[6] found that at 280°-300° the limit of esterification with equimolar quantities of acid and alcohol was from 69-72 per cent, somewhat higher than the equilibrium found by Berthelot and Paen de St. Gilles in liquid systems Milligan, Chappell, and Reid, on the other hand, found much more complete conversion in the gaseous phase, using silica gel as catalyst. Edgar and Schuyler[7] showed that the equilibrium is much more nearly complete conversion in the vapour phase than in the liquid condition, as determined by distilling equilibrium mixtures. This is in accord with Milligan, Chappell, and Reid. It is, however, as has already been pointed out, in disagreement with the observations of Sabatier and Mailhe that the reverse process of hydrolysis occurs to the extent of 30 per cent in equimolar mixtures of ester and water. Further experimental work is here necessary.

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[1] *Bull. Soc Chim.*, 1921, **29**, 101.

[2] *J. Physical Chem*, 1924, **28**, 872.

[3] *Chem. Zeit.*, 1913, **37**, 146.

[4] *J. Amer. Chem. Soc.*, 1922, **44**, 385, 2175, 1923, **45**, 809, 1924, **46**, 130, 1925, **47**, 807.

[5] *Trans. Farad. Soc.*, 1922, **17**, 607.

[6] *Loc. cit.*

[7] *J. Amer Chem. Soc.*, 1924, **46**, 64.

Dehydration of alcohols and ammonia yielding amines—Alcohol vapours and ammonia when led over oxide catalysts undergo dehydration, the elements of water being removed from the two reactants jointly, according to the equation

$$C_nH_{2n+1}OH + NH_3 = H_2O + C_nH_{2n+1}OH$$

Investigations of Sabatier and Mailhe [1] have shown that this process is generally applicable in the synthesis of amines It is produced readily in presence of thoria at temperatures of 300°-350° without production of ethylenic hydrocarbon With the other oxides cited in the earlier table as possessing mixed dehydrating and dehydrogenation properties, the production of amines is equally possible without accompaniment of ethylenic hydrocarbon or hydrogen as side products The formation of amine completely predominates

By substitution of a primary amine for ammonia in the entering vapours, the product obtained is a secondary amine

$$R.OH + R_1\ NH_2 = R_1N.HR + H_2O$$

This forms a general method for the preparation not only of symmetrical secondary amines -which result in small quantity as a secondary reaction in the dehydration of ammonia and alcohol but also of mixed secondary amines [2] Thus, from ethyl alcohol and isoamylamine, secondary ethyl isoamylamine is readily obtained Similarly, also, alkyl derivatives of piperidine may be obtained [3]

With phenol reaction is very small,[4] even at 400° With β-naphthol, however, reaction with ammonia occurs in contact with alumina in the temperature interval 300°-550° C, with the production of β-naphthylamine [5]

Dehydration of alcohols and hydrogen-sulphide yielding thiols - By a procedure analogous to that just detailed for the synthesis of amines, it is possible to effect the synthesis of thiols The dehydration of alcohols admixed with sulphuretted hydrogen by means of oxide catalysts at temperatures in the interval of 300°-380° forms a general method of preparation of thiols from the corresponding alcohol

$$C_nH_m\ OH + H_2S \longrightarrow C_nH_m\ SH + H_2O$$

The reaction may be accompanied by further dehydration of thiol and alcohol to produce the corresponding sulphide, according to the equation

$$C_nH_m\ SH + C_nH_m.OH = (C_nH_m)_2S + H_2O\ ^6$$

Of the oxide catalysts employed, thoria has proved the best, the yields of thiol with the simpler primary aliphatic alcohols exceeding 75 per cent The side reaction producing ethylenic hydrocarbon is small in such cases, but with secondary alcohols it is considerable, and the yields seldom exceed 30 per cent.

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[1] *Compt rend*, 1910, **150**, 823

[2] Sabatier and Mailhe, *Compt rend*, 1909, **148**, 900

[3] Gaudion, *Bull Soc Chim*, 1911 (iv), **9**, 417

[4] Sabatier Reid, p 284

[5] Lowy and Howald, U S P 1449423

[6] Sabatier and Mailhe, *Compt rend*, 1910, **150**, 1220

The yield of thiol per 100 parts of isoamyl alcohol decomposed decreases with the oxide catalyst employed to the extent shown in the following table :

ThO_2	70	W_2O_3	22
ZrO_2	44	Cr_2O_3	18
UO_2	30	Mo_2O_5	17
..	..	Al_2O_3	10

With the catalytic agents of small efficiency the product is mainly amylene.

Phenols at a somewhat higher temperature range of 130°–180° yield the corresponding aromatic thiols :

$$C_6H_5.OH + H_2S = C_6H_5.SH + H_2O,$$

but only in small quantities, the yields never exceeding 10 per cent.[1]

Dehydration of aldehydes and ketones.—Condensation of several molecules of aldehydes or ketones, with simultaneous elimination of water, is promoted by various dehydrating agents common in organic technique such as sodium or potassium hydroxide, sodium acetate, dry hydrogen chloride, zinc or aluminium chlorides.

In the case of aldehydes, the product is in general a higher unsaturated aldehyde, as, for example, in the case of acetaldehyde, which is slowly transformed by boiling with aqueous sodium acetate or zinc chloride into crotonic aldehyde, according to the reaction (see also p. 359)

$$CH_3.CHO + CH_3.CHO \longrightarrow CH_3.CH:CH.CHO + H_2O.$$

The analogous reaction with acetone is provided by reagents such as aluminium chloride, sodium, or lime, yielding, even in the ordinary temperature with long contact, mesityl oxide in the first place, and then phorone :

$$2CH_3.CO.CH_3 \longrightarrow (CH_3)_2:C:CH.CO.CH_3 + H_2O \longrightarrow$$
$$(CH_3)_2:C:CH.CO.CH:C(CH_3)_2.$$

Condensation with elimination of water between mixed aldehydes and ketones is similarly possible, especially with aromatic aldehydes. Thus :

$$(1)\ C_6H_5.CHO + CH_3.CO.CH_3 \longrightarrow C_6H_5.CH:CH.CO.CH_3 + H_2O,$$

$$(2)\ 2C_6H_5.CHO + CH_3.CO.CH_3 \longrightarrow (C_6H_5.CH:CH)_2CO + 2H_2O.$$

The variations of this reaction are manifold, and the agencies employed have likewise been multiplied in organic synthesis—generalisation or systematisation of the change is impossible, since they have been little studied from the theoretical point of view—doubtless due in a degree to the slowness of the reaction velocity

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[1] Sabatier and Mailhe, *Compt. rend.*, 1910, **150**, 1570.

Dehydration of alcohol-aldehyde mixtures yielding acetals.—Dry hydrogen chloride is the normal catalytic agent[1] for simultaneous dehydration of mixtures of alcohol and aldehyde, the product of reaction being the acetals The aldehyde is added to a 1 per cent solution of hydrogen chloride in the alcohol and reaction is allowed to take place in the cold

$$R\cdot CHO + 2R'\cdot OH \longrightarrow R\cdot CH(OR')_2 + H_2O$$

If heat be employed to accelerate the reaction, the yields diminish owing to the hydrolytic influence on the product of the catalyst employed The same catalytic agent promotes the action of aldehydes and alcohols to form acetals with the simultaneous employment of ethyl orthoformate

Simultaneous dehydration and elimination of carbon dioxide from acids, yielding ketones. With the aid of oxide catalysts, the fatty acids higher than formic acid yield, on heating, symmetrical ketones with simultaneous elimination of water and carbon dioxide

$$2R\cdot COOH \longrightarrow R\cdot CO\cdot R + CO_2 + H_2O$$

As is well known, dry distillation of the calcium or barium salts of the fatty acids yields the corresponding ketone The transformation of this process to a catalytic reaction was suggested by Squibb[2] who proposed to pass the vapour of acetic acid over barium carbonate heated to 500° As early as 1902 this process, according to Conroy[3] was said to be applied industrially, yields of more than 90 per cent being possible In the later of the two papers cited Squibb records the decomposition to 90 per cent acetone of 1700 lbs of absolute acetic acid in a large rotatory still 12 feet long by 2 feet diameter during a period of 126 hours This would correspond with a conversion of approximately one-third of a pound of acetic acid per cubic foot of atalyst space per hour Precipitated carbonate constitutes an efficient atalyst, [illegible]action being rapid at 450° The activity of the catalyst is of ong duration, in spite of slight carbonisation, and naturally at such emperatures in the presence of such a partial pressure of carbon dioxide xists entirely in the form of carbonate

Ipatiew and Sch[illegible]lmann[4] and Mailhe[5] extended the list of catalysts o zinc oxide and carbonate, cadmium oxide, and chromium oxide, whilst Senderens[6] showed that alumina and thoria operated efficiently n the neighbourhood of 350°-400° The yields are high, and the activity s constant, in the case of thoria revivification of the catalyst can be effectually carried out by simple ignition. Adkins and Nissen[1] have shown that the rate of reaction is not sensitive to the methods of preparation of the alumina catalyst, a feature already discussed in the case of dehydration of amides.

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[1] E Fischer and Groebe *Ber*, 1897, **30**, 3053

[2] *J Amer Chem Soc*, 1895 **17**, 187, 1896 **18**, 231

[3] *J Soc Chem Ind*, 1902 **21**, 309

[4] *J Russ Phys Chem Soc* 1904, **36**, 764

[5] *Mémoire Ac des Sc Toulouse*, 1907

[6] *Bull Soc Chim*, 1908 (iv), **3**, 824

Ferrous oxide is a suitable catalytic agent for the production of ketones from the higher fatty acids. Thus, with stearic acid, an 80 per cent yield of stearone may be obtained.

Modern plants for the manufacture of synthetic acetone employ such catalytic agents, with economies in the operating temperatures and in the yield of product. Thus, it is possible, by means of a three-stage process, each stage catalytic in nature, to proceed from alcohol to acetone. The conversion of alcohol to aldehyde is a typical dehydrogenation process, as earlier outlined. Oxidation of aldehyde yields acetic acid, and dehydration of this with elimination of carbon dioxide results in acetone. The possibilities elsewhere outlined for production of alcohol on the technical scale by catalytic processes, taken in conjunction with the present application, illustrate in a marked manner the penetration of the catalytic reaction into modern industry.

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[1] *J. Amer. Chem. Soc.*, 1924, **46**, 130.

CHAPTER XIII

COLLOIDAL CATALYSTS

We have had occasion to note that in the preparation of active catalysts the reactants were frequently converted into the colloidal form before drying at low temperatures, in order to ensure a large specific and active surface Again, the employment of catalysts in the form of finely divided materials precipitated on catalyst supports, *e g* platinum black on magnesium sulphate or platinum sheet, is now quite general In addition to these two forms, in which catalysts have been employed as agglomerated colloids, we find that for certain purposes colloidal suspensions and emulsions of catalytic substances present great advantages

As representative of these types we may consider both the colloidal metals—especially platinum, palladium, and nickel—and the enzymes These two possess certain characteristics in common, and for which reason the term inorganic ferments has been applied by Bredig[1] to colloidal metal sols

Colloidal Metals

Ritter and H Davy first made use of cathodic dispersion methods for the preparation of metallic sols, which method has now been supplanted by those of Bredig and Svedberg[1]

For the preparation of pure hydrosols the electrical methods offer certain advantages over chemical processes, such as reduction with phosphorus (Faraday), formaldehyde (Zsigmondy), hydrazine (Gutbier), acrolein (Castoro), or protalbinic and lysalbinic acids (Paal), in that impurities which may act as protective colloids or as precipitating electrolytes are entirely eliminated Reduction with hydrogen[2] or carbon monoxide[3] produces purer sols than the previously mentioned chemical reduction processes, but are not so good as the methods of electrical dispersion.

The following diagrams illustrate Bredig's and Svedberg's methods for the preparation of hydrosols and organosols of the metals

[1] *Methoden zur Herstellung Kolloider Losungen*, Dresden, 1909

[2] Kohlschutter, *Zeitsch. Elektrochem*, 1908, **14**, 49

[3] Donau, *Monatsch*, 1905, **26**, 525, 1906, **27**, 71.

In Bredig's method of preparation, an electric arc (4-10 amperes at 50-220 volts) is struck between two thin wires of the metal under the liquid. The wires should not exceed 2 mm. in diameter and the optimum arc gap is usually only 1 or 2 mm. in length.

Silver, gold, platinum, and iridium sols can easily be prepared by this method. The addition of a trace of alkali yields a better sol, but, for many purposes, electrolytes must be entirely eliminated. The process is in reality one of cathodic dispersion, since the anode frequently gains somewhat in weight during sol formation. For metals which are somewhat easily oxidisable, such as lead, cadmium, and copper, the water must not contain any oxygen, and the sol should be prepared in a hydrogen or nitrogen atmosphere.

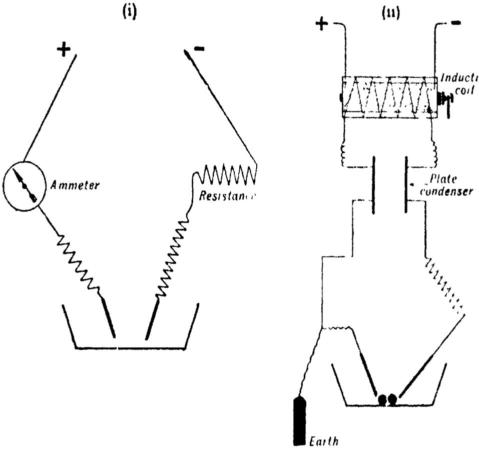

FIG. 19.

Metals such as zinc or iron yield hydroxides when attempts to prepare hydrosols are made. Organosols in methyl, ethyl, and especially isobutyl alcohols, ethyl malonate, ether, chloroform, or hydrocarbons, when prepared by Bredig's method, are usually very impure, containing large quantities of carbon produced by decomposition of the dispersion medium.

Svedberg introduced a method which yielded much purer organosols than could be produced by the direct arc process, utilising a high-tension oscillating spark discharge for the dispersion of his electrodes (6-inch spark coil). By the introduction of a high-capacity inductance into the circuit and keeping both the self-inductance and resistance of the circuit as low as possible, both hydrosols and organosols of high purity could be obtained The metal for dispersion forms both electrodes, and small pieces of the same metal may be placed at the bottom of the containing vessel, since, owing to the high voltage of the applied current sparks may be formed over several inches of the vessel between neighbouring pieces of metal

Less than 2 per cent of carbon is usually introduced when an organosol, *e g* isobutyl alcohol sol, is prepared in this manner By slight modification of Svedberg's method even non-metals of poor conductivity may be dispersed Svedberg has prepared organosols of such elements as sulphur, phosphorus, carbon, and silicon, as well as of certain minerals, such as copper sulphide A high degree of dispersity has readily been attained

The hydrosols thus prepared are usually negatively charged, although certain metals, especially iron and bismuth, are positive, owing, doubtless, to the presence of hydroxides, which in the sol form are usually positive

The differences of potential between sol and dispersion medium are small Thus Burton[1] gives the following figures

Dispersion Medium	Sol	E in Volt
Ethyl malonate	Pt	0 054
	Au	- 0 033
Ethyl alcohol	Ag	- 0 040
	Pt	0 024
Methyl alcohol	Zn	+ 0 015
	Pb	0 046

The average electric charge on a particle of silver sol is, according to the same investigator, about 2 8 × 10^{-2} electrostatic units, or for one gram-equivalent of silver in the dispersed state the charge is only 4 per cent of the charge on a gram-equivalent Both charge and sign naturally vary when electrolytes are added to the dispersion medium, and, as in other colloidal systems, the usual phenomena of precipitation and adsorption are noticed

In preceding pages we have already noted the application of colloidal metals to catalytic operations, but the striking resemblances of the colloidal metallic sols to organo-enzymes are most convincingly demonstrated by their behaviour in the catalytic decomposition of hydrogen peroxide, which subject has been minutely investigated by Bredig and his co-workers

Very small concentrations of the metal sol are able to influence catalytically the rate of decomposition of hydrogen peroxide solutions. Thus, Bredig obtained the following values for a minimum observable catalytic influence

Metal Sol	Dilution 1 gram atom per
Pt	70 10^{8} litres
Pd	26 10^{6} ,,
Au	1 10^{6} ,,

---

[1] *Phil Mag*, 1904 **6**, 7425 *et seq*

Some colloidal metallic oxides were also observed to have a feeble catalytic influence.

A high dispersity in the sol is naturally a desirable feature for enhanced activity, as, under these conditions, the maximum surface per unit mass of substance is obtained, and, at the same time, both the increase in the diffusivity and in the Brownian movement permit of a greater frequency of contact.

This increase of Brownian movement with increase in dispersity is well exemplified in the following figures obtained by Zsigmondy for gold sols:

Diameter in $\mu\mu$	Amplitude in μ
6	> 10
10	3·4
35	1·7

How far ultimate subdivision from $5\mu\mu$, the lower limit of the ultramicroscope, to molecular dimensions $0{\cdot}0002\mu$ increases the catalytic activity is uncertain, since no method of size measurement for these amicrons has yet been proposed. Qualitatively, however, it has been shown that the catalytic activity of a definite quantity of colloidal gold in the decomposition of hydrogen peroxide first rises and then falls as the extent of subdivision is increased.

The catalytic action of colloidal platinum. The reaction kinetics of the decomposition of hydrogen peroxide by platinum, both in the colloidal and in sheet form, has been the subject of numerous investigations. Bredig[1] and his co-workers showed that over a fair range of concentration the reaction proceeded according to a unimolecular law[2] This type of reaction is to be anticipated on the diffusion layer hypothesis of Nernst, Noyes, Whitney, and Brunner,[3] where the reaction velocity at a surface which is governed in speed by the ratio of diffusion of the reactant to that surface, through an adhering film, is given by

$$\frac{dx}{dt} = \frac{DA}{\delta v}(a - x),$$

where D is the diffusion coefficient, A the area, δ the film thickness, and v the volume of solution.

The serious objections to this view arise from the fact that the temperature coefficient is found to be relatively large, *circa* 1·7 for 10° rise. Again, the vigorous evolution of oxygen gas, as well as the rapid Brownian agitation, would be expected to modify very considerably the conditions postulated by Nernst for the establishment of the diffusion layer.

The problem arises in a new form from a consideration of the work of Teletow,[1] who noted that the rate of decomposition at the surface of a rotating platinised platinum surface followed the unimolecular law, the velocity constant being dependent on the rotation speed, in accordance with the following equation:

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[1] *Zeitsch physikal Chem*, 1899, **31**, 258; *ibid*, 1901, **37**, 1; 1901, **37**, 323 *Ber*, 1904, **37**, 798

[2] *Zeitsch physikal. Chem*, 1897, **23**, 689.

[3] *Ibid*, 1904, **47**, 52; 1900, **35**, 282.

$$K = an^{\frac{2}{3}}$$

The temperature coefficient was found to be 1·28 These experiments have been extended by Smith and Rideal, who find that the reaction velocity rises to a well-defined maximum with the rotation speed and that the temperature coefficient for the maximum velocity above 25° C is 1·28, but is smaller below this temperature. It is clear that the diffusive hypothesis alone is by no means adequate to explain these limiting velocities

If large quantities of platinum sol be employed, the reaction velocity is apparently somewhat greater than unimolecular, for the "constant" rises during the reaction Denham[2] and MacInnes[3] suggested that diffusion was not the limiting factor, but that hydrogen peroxide was adsorbed by the platinum and that the reaction velocity was proportional to the adsorbed quantity The quantity adsorbed is related to the bulk concentration by the Freundlich isotherm equation, and thus we obtain

$$\frac{dx}{dt} = k(a - x)^{\frac{1}{n}}$$

or

$$K = \frac{n}{t(n-1)}\left[a^{\frac{n-1}{n}} - (a-x)^{\frac{n-1}{n}}\right]$$

The agreement obtained in certain cases is excellent, as is evident from the following figures

2·0 mg Pt per litre $a = 0·0972$ mol H_2O_2 per litre

t min	$a - x$	k uni	k above eqn
0	0·0972		
6·03	0·0685	58	27
11·42	0·0475	63	28
15·85	0·0337	67	28
21·18	0·0219	70·5	28
26·70	0·0139	73	27
32·10	0·0079	76	27

A similar expression was found to obtain by Blackadder[4] for the decomposition of dilute formic acid at the surface of rhodium, and by

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[1] *Zeitsch Elektroche*[illegible]06, 12, 581

[2] Diss., Heidelburg, 1909

[3] *Amer Chem Soc*, [illegible]6, 878

[4] *Zeitsch physikal Chem.*, 1912, **81**, 385

Sieverts and Peters[1] for the decomposition of sodium hypophosphite at a surface of palladium sponge. It is clear that in strong solutions the surface of the colloidal platinum will be covered, at least in respect to its active area, with a unimolecular layer of hydrogen peroxide, and the reaction velocity will thus be of zero order over a wide range, from the critical value, where almost complete saturation is attained to very strong solutions. Some of Bredig's data, especially in alkaline solution, conform to this law.

On this assumption the marked divergence in temperature coefficients between colloidal platinum and rotating platinised sheet is not easy to understand. It is not necessarily conclusive that the low temperature coefficient of 1·28 for massive rotating platinum is indicative of a diffusive mechanism. It is indeed more probable that the large temperature coefficient of 1·7 for colloidal platinum is fictitious.[2] It is found, for example, that the reaction velocity is markedly affected by the addition of alkali. Two quite distinct effects may be noted. If small additions of alkali be made (0·1 millimol per litre), the activity is found to rise to a maximum and then sink, the reaction velocity still being unimolecular, as is clear from the following table:

Pt content, 0·64 mg./litre

Millimols NaOH per Litre	Half Life of the Peroxide in Minutes	Relative Activity
0	255	9
0·002	34	65
0·0078	24	92
0·031	22	100
0·125	34	65
0·250	70	31·5
0·500	162	13·5
1·00	520	4·2

On further addition of alkali the reaction velocity commences to rise again, but the reaction is now of zero order. An optimum is noted at 0·03*n*. It is probable that the small additions of alkali in increasing the reaction velocity are due to a peptising or disintegrating action on the colloidal metal. A similar peptising action has been, in fact, observed for several substances, such as charcoal and other metals, whilst sheet platinum is readily rendered catalytically active by treating with relatively concentrated caustic alkalis. The maximum of disintegration is obtained at about 0·125 millimol per litre, subsequent recoagulation occurring with a diminution in activity. Increase in temperature may well increase dispersion, resulting in the anomalous high value for the temperature coefficient of the reaction. In strongly alkaline solutions, salts of hydrogen peroxide are formed, e.g. NaOOH,[1] of which the ion OOH′ would appear to be extremely reactive.

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[1] *Zeitsch. physikal. Chem.* 1916, **91**, 199.

[2] Senter, *Zeitsch. physikal. Chem.*, 1903, **44**, 257; 1905, **51**, 673.

Tryhorn and Jessop[2] have examined the decomposition of peroxide on colloidal cobaltic hydroxide and find a similar rise in velocity on the addition of alkali up to 20 millimols of ammonia per litre, an optimum being obtained at about 9.8 millimols of ammonia per litre.

These investigators have not considered the possible influence of ammonia in peptisation of the active surface, but ascribe the increase in velocity to the following mechanism. Hydrogen peroxide is assumed to be adsorbed at a rate proportional to the bulk concentration, $\alpha_1 c_1$. The adsorbed hydrogen peroxide is assumed to undergo partial ionisation, e.g. $PtHO_2'x - \dot{H}$, the hydrogen ion being removed by a hydroxyl ion in the solution. The rate of such removal will be $\alpha_2 c_2$, where c_2 is the bulk concentration of hydroxyl ions.

The adsorbed O_2H' ions now undergo decomposition, regenerating hydroxyl ions and oxygen atoms which combine and are liberated at a rate α_3.

If the fraction of active surfaces respectively unoccupied, covered with O_2H' ions and with peroxide molecules be θ_3, θ_2, and θ_1 respectively.

When a steady rate is reached,

$$\alpha_1 c_1 \theta_3 = \alpha_2 c_2 \theta_1 = \alpha_3 \theta_2,$$

also

$$\theta_1 + \theta_2 + \theta_3 = 1,$$

the rate of gas evolution will be

$$\frac{\alpha_3 \theta_2}{2} = \frac{\delta x}{\delta t},$$

or eliminating θ_1 and θ_2 and θ_3, we obtain

$$\frac{2\,dx}{dt}\left|\frac{1}{\alpha_1 c_1} + \frac{1}{\alpha_3} + \frac{1}{\alpha_2 c_2}\right| = 1$$

Writing for c_1 equal to $a - x$, we obtain

$$\frac{a - x}{dx/dt} = \frac{1}{kA} = \frac{2}{A}\left|(a - x)\left(\frac{1}{\alpha_2 c_2} + \frac{1}{\alpha_3}\right) + \frac{1}{\alpha_1}\right|$$

which agrees with the experimental data.

The rate of surface decomposition of hydrogen peroxide is probably affected by the nature of the platinum oxide which may be present on the surface. Euler[3] states in fact that platinum black freed from oxygen exerts no catalytic activity on the decomposition of the peroxide. The electrolytic oxidation of formic acid likewise proceeds at, and only at, two definite potentials of the electrode at which definite oxides are assumed to be formed, indicating two different reaction mechanisms for this surface oxidation process. The abrupt change in the temperature coefficient of the rate of decomposition of hydrogen peroxide at a rotating platinised surface likewise takes place where one oxide is converted into the other.

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[1] Calvert, *Zeitsch physikal Chem* 1901 **38**, 513

[2] *J Chem Soc*, 1925, **127**, 132

[3] *Wied Ann* 1900, **24**, 949

The effect of poisons on colloidal and massive catalysts has already been referred to (Chapter VI.)

Bredig's values for the inhibiting or poisoning influence of small quantities of hydrocyanic acid on platinosol are shown in the following curves:

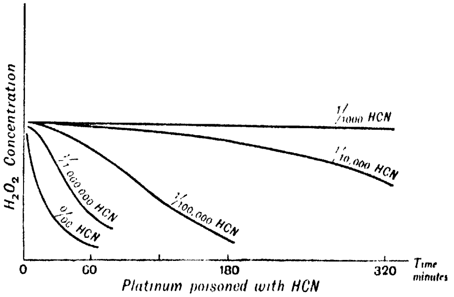

FIG 20.

whilst the following concentration of poisons can be detected by their inhibiting influence on the decomposition of peroxide of hydrogen by platinosol:

Poison.	Concentration.
HCN	$1 : 20 . 10^6$
KCN	$1 : 3 . 10^6$
I_2	$1 : 7 . 10^6$
$HgCl_2$	$1 : 2{\cdot}5 . 10^6$ [1]

The action of carbon monoxide is an interesting one. It is an active poison for colloidal platinum in the decomposition of hydrogen peroxide, but does not affect manganese dioxide or organic catalysts.

Frequently poisoning is not absolute, and the catalyst is able to recover from poisoning and exert its normal activity once more. Bredig made the interesting observation that platinum poisoned with carbon monoxide is frequently more active, after its recovery, than platinosol not subjected to this treatment.

The effect of poisons is also a case of selective action. Thus hydroxylamine and potassium nitrate poison liver catalase, activate a silver sol, and are without action on platinosol It is to be expected, as is indeed the case, that the halides, cyanides, and sulphides should act as poisons for a silver sol owing to the formation of a definite insoluble film on the surface of the colloid particles The poison itself, as in the case of iodine, may also exert a catalytic activity *per se*

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[1] See also Titof, *Zeitsch. physikal. Chem.*, 1903, **45**, 611; Raschig, *Chem. Zeit*, 1907, **31**, 926; and Chap. II.

Bredig has attempted to carry the analogy between colloidal metals and enzymes still further, pointing out that the preparation of mercury sol or that of manganese dioxide by the addition of gold or hydroxyl ions is comparable to the transformation of a proenzyme into an enzyme

The decomposition of hydrogen peroxide at the surface of colloidal platinum is a representative example of reactions taking place in liquid media at colloidal surfaces The hydrogenation of organic substances

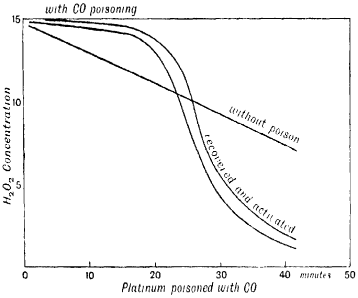

FIG. 21

by colloidal metals likewise presents points of interest in that other factors are involved

We have already noted the evidence in favour of the hypothesis that both hydrogen and the organic substance undergoing hydrogenation are adsorbed at the surface of the catalyst and the influence of the nature of the organic substance on the rate of hydrogenation under specified conditions The effect of hydrogen pressure and rate of agitation of the solution on the reaction velocity have been investigated by Rideal,[1] and present features somewhat akin to those noted in the decomposition of hydrogen peroxide If relatively large quantities of active catalyst be present in the solution, the rate of hydrogenation for a feebly agitated solution is found to be a zero order reaction We are in fact measuring the rate of diffusion of the hydrogen to the colloidal catalyst If the shaking speed of an oscillating hydrogenation vessel be increased, the reaction velocity constant is found to increase as the square of the velocity of shaking, or

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[1] *Trans Farad Soc*, 1923 **19**, 1

$$\frac{\delta x}{\delta t} = Kn^2.$$

every oscillation of the shaker presents a fresh gas liquid interface and the thickness of the liquid film round each particle is dependent on the rate of the movement of the particle.

That the velocity of diffusion of hydrogen governs the rate of hydrogenation was confirmed by the observation that sodium cinnamate and phenyl propiolate underwent hydrogenation at the same rate.

If the quantity of active catalyst in colloidal suspension be reduced, in the particular 50-c.c. vessel containing 10 c.c. of solution, to less than 5 mg., the reaction in solution proceeds more slowly, and the solution is consequently not denuded of hydrogen as rapidly as it can be supplied. For small concentrations of colloidal palladium, *e.g.* 2 mg. per 10 c.c., the rate of reaction was found to be independent of the shaking speed, the solution thus being saturated with hydrogen. The reaction was again found to be of zero order, but the sodium phenyl propiolate solutions absorbed hydrogen at twice the rate that the sodium cinnamate solutions reacted. Both these salts were found to be adsorbed by the catalyst. Thus, one must conclude that both salts underwent reaction to form the completely saturated sodium dehydrocinnamate at the same speed, the treble-bond compound taking up 2 molecules of hydrogen at the same speed as the double-bond cinnamate takes up 1 molecule. A similar reaction has been noted by Hopkins, Morgan, and Stewart[1] in the case of the oxidation by methylene blue of hypo-xanthine and xanthine to uric acid at the surface of an enzyme, oxidase, present in liver tissue. When, however, mixed unsaturated substances undergo simultaneous hydrogenation we have noted the mechanism becomes more complicated. A study of the rates of hydrogenation of mixtures of these simple salts is evidently desirable.

For fresh active sols the reactions appear to be of zero order, and, as in the case of the decomposition of hydrogen peroxide, we may assume that the reactant is selectively adsorbed and strongly adsorbed, forming a saturated layer. Only towards the end of the reaction does the surface cease to be saturated and the reaction velocity begin to fall off. With old sols, on the other hand, the adsorptive capacity is weaker; thus, the surface is not saturated even in strong solutions and the reaction velocity curve becomes degraded to a form approximating to the unimolecular form obtained with dilute solutions of hydrogen peroxide at a relatively inactive platinum surface.

Some interesting cases of rhythmic or pulsating catalytic reactions may be mentioned. Ostwald[2] directed attention to the fact that the evolution of hydrogen from the solution of chromium in various solutions was not in a continuous stream, but came off in periodic bursts If the volumes liberated per minute were plotted against the time, a regular sinuous curve was obtained (Fig 22)

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[1] *Proc. Roy. Soc.*, 1922, **94**, 110.

[2] *Zeitsch. physikal. Chem.*, 1900, **35**, 33.

Bredig and Weinmayr,[1] in search of analogies with vital processes, were struck with the regular periodicity of this reaction, and compared it with that of a cardigram, or pulse curve They subsequently noticed that a similar pulsating effect was obtained in the liberation of oxygen from hydrogen peroxide when exposed to a surface of clean mercury

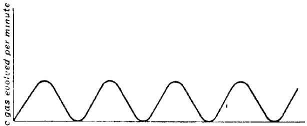

Fig. 22

As in the case of the beating heart, the rate of liberation of oxygen from the mercury surface is influenced by the addition of small quantities of various substances, especially colloids, very small concentrations of hydrion or hydroxylion, and certain electrolytes such as sodium acetate or ammonium citrate The extraordinary alteration in the character of the curve on the addition of a small quantity of ammonium citrate is well exemplified by the following example

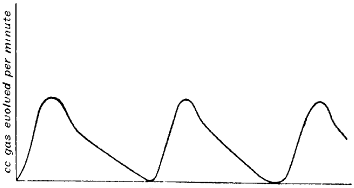

Fig. 23

It will be noted that the simple sinuous character of the curve has been entirely destroyed

The enzymes.— The enzymes must be regarded as colloidal catalysts As in the case of other heterogeneous reactions, the reactants are adsorbed by the enzyme in order that reaction may ensue The chief and most remarkable characteristic of enzyme action is their almost specific character, and the view must be adopted that, in the large complex organic aggregate forming an enzyme particle, certain specific groups are present to which the reactants are attached. The "molecular" weights of the enzyme aggregates are large, *e.g.* invertin is of the order of 19,600[1] to 25,000,[2] being comparable to those of dialysed albumin, 33,000. It is found that enzymes are strongly adsorbed by a variety of substances such as charcoal, alumina, fats, cholesterin, and calcium oleate. The effect of such adsorption on the activity of enzymes presents several interesting features. In some cases, *e.g.* in the adsorption of invertin by alumina,[3] the catalytic activity of the enzyme is unaffected by adsorption: the reactive groups which play a part in the adsorption are evidently not those which cause the hydrolysis of sugar, and which must be orientated in the solution in a direction away from the adsorbing alumina. In other cases adsorption renders the enzyme inactive or the chemically active groups must be also playing a part in effecting the union between enzyme and colloid, and thus turned in towards the adsorbent. Pancreas lipase is inert when adsorbed on cholesterin and partly active when adsorbed on alumina.

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[1] *Zeitsch physikal Chem*, 1903, **42** 601

The inert adsorbing material may in some cases accelerate the reaction between enzyme and reactant, a higher reaction velocity being obtained in the hydrolysis of fats by lipase when substances like calcium oleate or mixtures of calcium oleate and albumin are added.[4] It is possible in these cases to imagine that the adsorbent adsorbs both enzyme and reactant, thus increasing the total reaction velocity by augmentation of the "bulk" colloidal reaction with a surface reaction in a manner analogous to the acceleration produced by charcoal in the interaction between potassium iodide and dibromacids examined by Kruyt and van Duin.[5] The increase in the catalytic activity of calcium oleate on the velocity of reaction between enzyme and fat on the addition of albumin is analogous to the cases of catalytic promotion which we have discussed. We might regard the calcium oleate as adsorbing the fat more strongly than the lipase. Thus the surface action will not proceed at the optimum velocity. By the further addition of albumin, albumin-calcium oleate adsorption compounds are formed, on which the enzyme is strongly adsorbed by the albumin and the fat by the calcium oleate.

It is now generally assumed that the reaction velocity in enzyme processes is determined by the concentration of adsorption complex, reactant-enzyme, present in the system, a view first advanced in definite form by Bayliss[6] and elaborated by Armstrong,[7] Nelson,[8] Falk,[9] and others Whilst, according to Bayliss's view, the specificity of enzyme action is due to the specific and orientated nature of the adsorption process, Abderhalden and Fodor [1] believe that the subsequent catalytic and destructive processes are specific, the primary adsorption being common to all enzymes

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[1] Euler, *Zeitsch. physikal Chem.*, 1923, **130**, 87.

[2] *Zeitsch. physikal. Chem.*, 1911, **73**, 335.

[3] Nelson and Hitchcock, *J. Amer. Chem. Soc.*, 1921, **43**, 1956; Willstatter and Kuhn, *Zeitsch. physikal. Chem.*, 1921, **116**, 53.

[4] Willstatter, *Zeitsch. physikal. Chem.*, 1922, **125**, 93.

[5] *Rec. trav. chim.*, 1921, **40**, 249.

[6] *Biochem. Zeitsch.*, 1926, **175**, 1.

[7] *Proc. Roy. Soc.*, 1913, **86**, 378.

[8] *J. Amer. Chem. Soc.*, 1917, **39**, 790.

[9] *The Chemistry of Enzyme Actions*, New York, 1921.

The alteration of the hydrogen-ion concentration of the medium in general greatly affects the reaction velocity With impure and partly coagulated ferments, alteration in the P_H of the medium may alter the dispersity and thus the extent of active surface We have noted, however, that in certain cases, *e g* invertin when pure is unaffected by adsorption, and for such the alteration in velocity produced may be ascribed to a specific effect on the enzyme

The reaction kinetics of enzyme catalysis. Michaelis and Menten [2] first examined in detail the effect of variation of sugar concentration on the rate of inversion by invertin at a constant acidity of $P_H = 4{\cdot}6$, the reaction velocity is found first to rise to a maximum and thereafter sink with increasing sugar concentration It was found that the data could be expressed accurately in the form

$$\frac{ds}{dt} = K\frac{[S]}{[S]+K_s},$$

where $[S]$ is the concentration of free sugar, K_s a constant

If the original concentration of ferment be a and an amount b combines with sugar when the bulk concentration of sugar be $[S]$, we obtain by the law of mass action

$$[S](a-b) = K_s b \quad \text{or} \quad b = a\frac{[S]}{[S]+K_s},$$

where K_s is the dissociation constant of the complex sugar-ferment Since the reaction velocity according to our hypothesis is proportional to the amount of complex present, we obtain

$$\frac{ds}{dt} = K_s b = K\frac{[S]}{[S]+K_s},$$

in agreement with the observed data

K_s for the complex invertin sugar is found to be 0 0167 This value was confirmed at a later date by Euler and Laurin [3] by direct determination of K_s from the relationship

$$K_s = \frac{\text{Enzyme} \times \text{sugar concentration}}{[\text{Enzyme} - \text{complex}]}$$

In many cases the products of reaction are adsorbed, *e g* invertin adsorbs both cane sugar and fructose, the dissociation constants of the two complexes k_s for the cane sugar-invertin and k_f for the fructose-invertin complex may be determined by measuring the initial velocity of inversion of cane sugar in the presence of varying amounts of fructose. If the original amount of ferment present be a and b, and c be the amounts of the two complexes present in presence of amounts of sugar S and F, we obtain by the law of mass action

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[1] *Fermentforschung*, 1916 **1**, 533 1917, **2** 74, 1918, **2** 151 1920, **4** 191, 1919, **3** 193 1920, **4**, 204

[2] *Biochem Zeitsch*, 1913, **49**, 333

[3] *Zeitsch physikal Chem* 1919, **108** 64

$$[S][a-b-c]=K_S b,$$

$$[F][a-b-c]=K_F c,$$

whence

$$K_F=\frac{[F]\,K_S}{[S](a/b-1)-K_S}.$$

When the velocities without and with fructose present are v and v_1, clearly

$$\frac{v}{v_1}=\frac{b}{b_1}.$$

Where

$$b=\frac{a[S]}{[S]+[K_S]}$$

we thus obtain

$$K_F=\frac{[F]K_S}{[S+K_S](v/v_1-1)}.$$

In this way the following values have been obtained for invertin :

K cane sugar	0·0167	K fructose	0·057
K glucose	0·088	K mannose	0·083

Effect of hydrogen-ion concentration. The fact that enzymes are very sensitive to changes in the hydrogen ion concentration of the medium was first noted by Loeb[1] and investigated in detail by Michaelis and Davidsohn.[2] If the activity of an enzyme reactant system be plotted as a function of the P_H of the solution, it is noted that there exists a well-defined maximum of activity falling as the solution becomes more alkaline or more acid

In the case of the system saccharase-sugar the velocity decreases as the solution becomes more alkaline from P_H 4·5 and ceases at a P_H of *ca.* 9. The form of the curve, activity - P_H, is similar to that exhibited for the dissociation of a weak acid, being expressible in the form

$$\text{Activity}=K\frac{[\dot{\mathrm{H}}]}{[\dot{\mathrm{H}}]+K'},$$

K possessing the value for this particular system of $2\cdot 10^{-7}$.

This alteration in the activity with the P_H may readily be interpreted on the hypothesis that the enzyme possesses an acid dissociation constant of value $K = 2 \cdot 10^{-7}$, and that the ionic form is catalytically inactive, the undissociated molecule alone possessing catalytic activity. In cases where bases decrease the activity, the hypothesis of an amphoteric enzyme may be advanced

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[1] *Biochem. Zeitsch.*, 1909, **19**, 534

[2] *Biochem. Zeitsch.*, **1911, 35, 386** ; see also *ibid.*, 1914, **60**, 91 ; 1920, **110**, 217.

Since, however, the form of the relative velocity curve at constant P_H alters in a similar manner with alteration in the sugar concentration (see *ante*), the combination of the two factors leads to the expression

$$\text{Velocity} = \frac{K}{1 + S/K_s},$$

where K is the acid dissociation constant of the enzyme and K_s that of the complex, sugar-enzyme

It is found, however, that the velocity is at a P_H 6·7 independent over wide variations of the sugar concentration an experiment which casts some doubt upon the validity of the above assumptions

Kuhn[1] concludes that the amount of combination between enzyme and sugar is unaffected by a change in the P_H, and that the change in velocity is to be ascribed rather to the ionisation of the complex saccharose-saccharase, which can be regarded as a weak acid, the decomposition rate of which is affected by its ionisation

Euler[2] finds the dissociation constant of the enzyme invertin to be $K_a = 10^{-7}$, whilst the dissociation constant of the complex, invertin-sugar, is $K_a = 3 \cdot 10^{-7}$, they are thus both acids of the same strength

Sugars, according to Euler, are likewise slightly dissociated as acids and as bases, and their ionisation may affect the dissociation of the enzyme and the enzyme-sugar complex In general however, the sugars are of insignificant strength and their contribution of hydrogen ions may be neglected ($K_{\text{acid}} = 10^{-13}$ for saccharose and $K_{\text{base}} = ca\ 10^{-20}$)

According to this view, the reaction velocity in the system is proportional to the concentration of the undissociated complex sugar-enzyme, which is to be regarded as a weak acid or $\frac{dc}{dt} = K(HES)$

The following equilibria exist in solution containing hydrogen ions of activity [H], enzyme E and sugar S

$$(1)\ \frac{[HE][S]}{[HES]} = K_s \qquad (2)\ \frac{[\mathrm{H}][ES']}{[HES]} = K_a$$

$$(3)\ \frac{[\mathrm{H}][E']}{[HE]} = K_a' \qquad (4)\ \frac{[E'][S]}{[ES']} = K_s'$$

Euler assumes that in the regions where the K_s appears to be independent of the P_H, $K_s = K_s'$ or the sugar possesses the same affinity for the undissociated enzyme as for the ion of the enzyme Hence it follows also that $K_a = K_a'$

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[1] *Zeitsch physikal Chem*, 1922 **125**, 1

[2] *Zeitsch physikal Chem*, 1922, **120**, 61, *ibid*, 1923 **134** 39, *Ber*, 1923, **57**, 299

The total quantity (F) of saccharase present is accordingly:

$$F = [HES] + [HE] + [E'] + [ES'] = [HES]\left\{1 + \frac{K_s}{[S]} + \frac{K_aK_s}{[S][\dot{H}]} + \frac{K_a}{[\dot{H}]}\right\},$$

whence
$$\frac{dv}{dt} = k[HES] = KF\frac{[\dot{H}][S]}{[\dot{H}]([S] + K_s) + K_a([S] + K_s)}.$$

The percentage distribution of enzyme in an 0·2 molar sugar solution at P_H from 5 to 8 in the various forms has been calculated by Euler with the following results:

Form	P_H 5	P_H 6	P_H 7	P_H 8
$[HES]$	88	70	23	2·9
$[ES']$	2·6	21	69	87
$[HE]$	0·26	2·1	6·9	8·7

In many cases the acid ions alone are not the only effective enzymes; thus, we find that pepsin attacks albumin in the cationic form but trypsin the anions of the proteins. It would seem possible that some enzymes might attack proteins most readily at the isoelectric point where the acid and basic portions of the amphoteric protein are both equally dissociated. Thus, we find, according to Hertzmann and Bradley,[1] that pepsin attacks ovalbumin most readily at its isoelectric point.

Euler has made[2] many interesting comparisons between the catalysts invertin and hydrochloric acid in the inversion of cane sugar.

Since the basic dissociation constant of cane sugar is of the order of 10^{-20}, the concentration of complex $[\mathrm{H}][S]$ in 0·1 normal HCl will be of the order of 10^{-8}. This strength of acid is equivalent in inverting power to a $0{\cdot}6 \cdot 10^{-8}$ molar solution of the enzyme, which yields a substrate enzyme concentration of $[E][S]$ $0{\cdot}5 \cdot 10^{-8}$. The affinity constants of the two complexes being 10^{-6} and 50 respectively, it will be noted that the concentrations of active complex are practically identical, being produced in the case of the acid by a high concentration of acid with a low affinity, and in the case of the enzyme by a small concentration of enzyme possessing a great affinity.

The temperature coefficients of the two reactions are also markedly different: the energy of activation is found for acid inversion to be 25,600 cals.; for inversion by the enzyme only, 9400 cals.

The reaction velocity of enzyme actions. In many cases Schutz's law[3] is found to be obeyed in enzyme actions. Many proteins are readily hydrolysed by pepsin at a rate dependent on the quantity of pepsin present If an amount x of protein is hydrolysed during a time t by an amount of pepsin P, it is found that $x = K\sqrt{t}$ and $x = K'\sqrt{P}$, as the time or the enzyme concentration is chosen as variable, a combination of these two leads to Schutz's law, $x = K''\sqrt{Pt}$

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[1] *Proc. Amer. Soc. Biol. Chem.*, 1923, **18**, 19.

[2] *Zeitsch. physikal. Chem.*, 1900, **32**, 348; 1901, **36**, 641; 1904, **47**, 353; *Biochem. Zeitsch.*, 1920, **107**, 180.

[3] *Zeitsch. physikal. Chem.*, 1885, **9**, 577.

On squaring and differentiating with P as constant we obtain

$$\frac{dx}{dt} = \frac{K}{x}$$

This law, as pointed out by Langmuir,[1] follows immediately from the assumption that the product of hydrolysis (B) is capable of displacing the adsorbed reactant (A) Thus, if θ be the fraction of the surface covered with the reactant, the rest being covered with the product of reaction, equilibrium between the rate of replacement of reactant by the product is attained when

$$\alpha_B\mu_B\theta = \nu_B$$

and

$$\frac{dx}{dt} = \nu_A\theta$$

$$= \nu_A\left(\frac{\nu_B}{\alpha_B\mu_B}\right) = \frac{K}{x},$$

which is Schutz's law As example may be cited the data of Herzog[2] on the hydrolysis of ethyl acetate by a lipase present in pig's liver

Time	Quantity per cent hydrolysed	$K = \frac{x}{\sqrt{t}}$
5	3·5	1·6
10	5·8	1·8
15	7·0	1·8
20	7·8	1·7
30	10·1	1·8
[illegible]	12·8	1·9
[illegible]	14·4	1·9

[illegible]tion velocities have [illegible] the assumption [illegible]zyme-

and C, G, F be the concentrations of the three sugars, then, according to the law of mass action:

$$\begin{aligned}
&(1)\quad C(F - F_c - F_g - F_f) = K_c F_c,\\
&(2)\quad G(F - F_c - F_g - F_f) = K_g F_g,\\
&(3)\quad L(F - F_c - F_g - F_f) = K_f F_f.
\end{aligned}$$

From (1), (2), and (3) we obtain

$$(4)\quad F_c = C\frac{F - F_g - F_f}{C + K_c},\qquad F_f = F_c\frac{K_c F}{K_f C},\qquad F_g = \frac{K_f}{K_g}F_f,$$

and writing

$$\frac{1}{K_f} + \frac{1}{K_g} = q,$$

we obtain

$$F_g + F_f = K_c\frac{F}{C}q \cdot F_c.$$

Since the velocity is proportional to F_c, we obtain

$$\frac{dx}{dt} = KF_c = K\frac{FC}{C + K_c(1 + qF)}.$$

If x mols of sugar are hydrolysed, x mols. of glucose and fructose appear. Hence

$$\frac{dx}{dt} = K'\frac{a - x}{a - x + K_c(1 + qx)}.$$

On integration we obtain

$$K't = (1 - K_c q)x - K_c(1 + aq)\log(a - x) + \text{constant},$$

when $x = 0$, $t = 0$.

Hence the constant is

$$K_c(1 + aq)\log a.$$

Thus
$$K't = K_c(1 + aq)\log\frac{a}{a - x} + (1 - K_c q)x$$

or
$$\frac{1}{t}\left(\frac{1}{a} + \frac{1}{K_f} + \frac{1}{K_g}\right)a\log\frac{a}{a - x} + \frac{x}{t}\left(\frac{1}{K_c} - \frac{1}{K_f} - \frac{1}{K_g}\right) = K$$

It is clear that if the affinity of the products for the enzyme is the same as that of the reactant, or

$$\frac{1}{K_c} = \frac{1}{K_f} + \frac{1}{K_g},$$

the second term vanishes and we obtain a unimolecular constant. On the other hand, if the affinity of the reactant for the substrate is extremely large, the first term becomes small relative to the second, readily hydrolysed by pepsin at a rate dependent on the quantity of pepsin present. If an amount x of protein is hydrolysed during a time t by an amount of pepsin P, it is found that $x = K\sqrt{t}$ and $x = K'\sqrt{P}$, as the time or the enzyme concentration is chosen as variable, a combination of these two leads to Schutz's law, $x = K''\sqrt{Pt}$.

On squaring and differentiating with P as constant we obtain

$$\frac{dx}{dt} = \frac{K}{x}$$

This law, as pointed out by Langmuir,[1] follows immediately from the assumption that the product of hydrolysis (B) is capable of displacing the adsorbed reactant (A). Thus, if θ be the fraction of the surface covered with the reactant, the rest being covered with the product of reaction, equilibrium between the rate of replacement of reactant by the product is attained when

$$\alpha_B\mu_B\theta = \nu_B$$

and

$$\frac{dx}{dt} = \nu_A\theta$$

$$= \nu_A\left(\frac{\nu_B}{\alpha_B\mu_B}\right) = \frac{K}{x},$$

which is Schutz's law. As example may be cited the data of Herzog[2] on the hydrolysis of ethyl acetate by a lipase present in pig's liver.

Time	Quantity per cent hydrolysed	$K = \frac{x}{\sqrt{t}}$
5	3.5	1.6
10	5.8	1.8
15	7.0	1.8
20	7.8	1.7
30	10.1	1.8
45 25	12.8	1.9
60	14.4	1.9

The more general expressions for enzyme reaction velocities have been elaborated by Michaelis and his co-workers on the assumption that the reaction velocity is proportional to the quantity of enzyme-reactant complex present.

In the case of the inversion of cane sugar by saccharase, producing glucose and fructose, we obtain the following expressions.

If F = total amount of enzyme present,
F_c = amount of enzyme cane sugar complex of affinity constant K_c,
F_g = " " " glucose complex of affinity constant K_g,
F_f = " " " fructose complex of affinity constant K_f,

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[1] *J. Amer. Chem. Soc.*, 1916, **38**, 2292.

[2] Oppenheimer, *Die Ferm. und ihre Wirkungen* 4th edition, 1913, p. 10211

and C, G, F be the concentrations of the three sugars, then, according to the law of mass action:

$$(1)\quad C(F - F_c - F_g - F_f) = K_c F_c,$$
$$(2)\quad G(F - F_c - F_g - F_f) = K_g F_g,$$
$$(3)\quad L(F - F_c - F_g - F_f) = K_f F_f.$$

From (1), (2), and (3) we obtain

$$(4)\quad F_c = C\frac{F - F_g - F_f}{C + K_c}, \qquad F_f = F_c\frac{K_c F}{K_f C}, \qquad F_g = \frac{K_f}{K_g}F_f,$$

and writing

$$\frac{1}{K_f} + \frac{1}{K_g} = q,$$

we obtain

$$F_g + F_f = K_c\frac{F}{C}q \cdot F_c.$$

Since the velocity is proportional to F_c, we obtain

$$\frac{dx}{dt} = KF_c = K\cdot\frac{FC}{C + K_c(1 + qF)}.$$

If x mols of sugar are hydrolysed, x mols. of glucose and fructose appear. Hence

$$\frac{dx}{dt} = K'\frac{a - x}{a - x + K_c(1 + qx)}.$$

On integration we obtain

$$K't = (1 - K_c q)x - K_c(1 + aq)\log(a - x) + \text{constant},$$

when $x = 0$, $t = 0$.

Hence the constant is

$$-K_c(1 + aq)\log a.$$

Thus
$$K't = K_c(1 + aq)\log\frac{a}{a - x} + (1 - K_c q)x$$

or
$$\frac{1}{t}\left(\frac{1}{a} + \frac{1}{K_f} + \frac{1}{K_g}\right)a\log\frac{a}{a - x} + \frac{x}{t}\left(\frac{1}{K_c} - \frac{1}{K_f} - \frac{1}{K_g}\right) = K$$

It is clear that if the affinity of the products for the enzyme is the same as that of the reactant, or

$$\frac{1}{K_c} = \frac{1}{K_f} + \frac{1}{K_g},$$

the second term vanishes and we obtain a unimolecular constant. On the other hand, if the affinity of the reactant for the substrate is extremely large, the first term becomes small relative to the second, and the reaction becomes one of zero order Michaelis[1] obtained at 25° C at P_H 4.6 the following values

$$K_s = 0.0167, \qquad K_f = 0.058, \qquad K_g = 6.089,$$

whence
$$\frac{2.303}{t}(1+28a)\log\frac{a}{a-x}+\frac{32}{t}x=K$$

The values obtained for K are given in the following table

C in Molarity	K
0.33	0.0439
0.107	0.0445
0.0833	0.0465
0.0416	0.0445
0.0208	0.0474

Poisoning of enzymes. We have noted that enzymes, in common with colloidal metals, are extremely sensitive to poisons, which are adsorbed on the surface The mechanism of poisoning of enzymes has been investigated in detail by Euler and his co-workers[2] The following data showed the effect of addition of mercuric chloride to a solution of 60 c c 8 per cent sugar + 10 c c 4 per cent KH_2PO_4 + 1 c c containing 56 mg of invertin

$HgCl_2$ added mg	Relative Velocity of Inversion
0	100
0.03	100
0.06	78
0.15	39
0.30	20
0.61	8
1.5	2.5
3.0	2.0

The adsorption in this case is perfectly reversible as was shown by the almost complete recovery of the activity of the invertin on the addition of hydrogen sulphide In the same manner it was found that the activity of a partially poisoned enzyme could be restored by the addition of more cane sugar, the two adsorption compounds invertin-sugar and invertin-mercuric ion, competing for one another

In the following table are cited the concentrations of mercuric chloride necessary to reduce the activity of an invertin solution to definite fractions of its initial activity in the presence of varying concentrations of cane sugar

Sugar Conc in %	Mg $HgCl_2$ required to reduce the Activity to		
	50%	40%	33% of the Initial Value
8.0	0.09	0.13	0.15
16.0	0.20	0.30	0.36
24.0	0.29	0.45	0.54

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[1] *Loc cit*

[2] *Fermentforschung* 1920, **3** 330 *Zeitsch physikal Chem*, 1922, **121**, 177, *Zeitsch Exp Med*, 1923, **33**, 483, *Ber* 1922, **55** 416

Silver salts are even more efficacious than mercuric chloride in this respect, and on the assumption of equivalent combination between silver ion and enzyme 107·8 grms. of silver are found to inactivate 4000-5000 grms. of saccharase.

Whilst copper and lead salts are less effective than silver, they appear to behave in a manner similar to mercury in that increasing concentrations of sugar lowers their toxic power. Silver, on the other hand, is to be distinguished from these salts in that cane sugar exerts no protective action for silver poisoning, a result which leads to the conclusion that the ferment is not parted between the sugar and silver ion but that the silver reacts with the complex ferment-sugar. Various organic substances such as aniline and the alkaloids likewise effect reversible poisoning;[1] the nitrophenols, on the other hand, poison in an irreversible manner, forming compounds which no longer dissociate.

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[1] Bloch and Rona, *Biochem. Zeitsch.*, 1921, **118**, 185

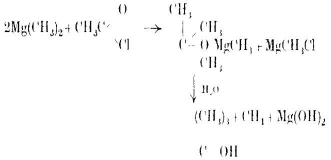
CHAPTER XIV

CATALYSIS IN ORGANIC CHEMISTRY

The Grignard Reagent

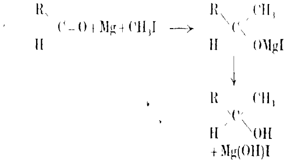
The use of organo-metallic compounds in organic synthesis may be said to date from the time of Frankland[1] and Cahours,[2] but it was not until Lohr isolated magnesium diethyl in 1890 that the development of synthetic operations by means of these reagents became generally possible

In 1893 Fleck performed the first synthesis with the new reagent, converting an acetyl chloride into a tertiary alcohol



$$2Mg(CH_3)_2 + CH_3C\begin{matrix}O \\ \\ Cl\end{matrix} \rightarrow \begin{matrix}CH_3 & \\ | & CH_3 \\ C - O\,MgCH_3 & \\ CH_3 & \end{matrix} + MgCH_3Cl \xrightarrow{H_2O} \begin{matrix}(CH_3)_3 \\ C-OH\end{matrix} + CH_4 + Mg(OH)_2$$

Barbier, in 1899, showed that it was unnecessary to isolate the magnesium alkyls for synthesis Thus, an aldehyde could be converted into a secondary alcohol by interaction with magnesium powder and an alkyl halide



$$\begin{matrix}R \\ H\end{matrix}\!>C=O + Mg + CH_3I \longrightarrow \begin{matrix}R & & CH_3 \\ & C & \\ H & & OMgI\end{matrix} \rightarrow \begin{matrix}R & & CH_3 \\ & C & \\ H & & OH\end{matrix} + Mg(OH)I$$

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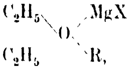
[1] *Annalen*, 1849 **71**, 203

[2] *Compt rend*, 1859, **49**, 1110

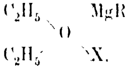
Grignard, Barbier's pupil, made the interesting discovery, a year later, that ether acted as a catalytic agent in the process, and that when this agent was present the reactions proceeded smoothly and good yields were obtained.[1]

All the metals of the uneven series of the Mendeléeff table yield organo-metallic compounds, with the exception of copper and silver, whilst calcium, potassium, and lithium of the even series also form similar compounds. Nevertheless, with the exception of the calcium alkyls, suggested by Beckmann[2] in 1905, magnesium is practically exclusively employed.

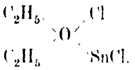
The mechanism of the Grignard reaction has not been definitely settled. Grignard himself showed that an additive compound was formed with the ether, $MgRX(C_2H_5)_2O$, and suggested the structural formula :



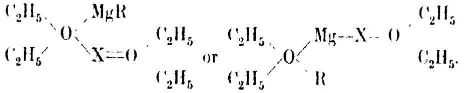
in the form of an oxonium compound Baeyer and Villiger suggested as alternative :



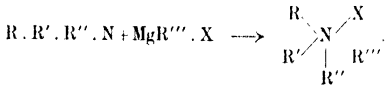
comparable with



Tschelinzeff,[2] in 1905, isolated MgRX by performing the operation in benzene solution, using a trace of ether as catalytic agent, and studied the heat of formation of the ether magnesium alkyl halide complex. He obtained the rather surprising result that apparently 2 molecules of ether took part in the reaction ($(C_3H_7MgI + Et_2O$ 6·63 kg cals $C_3H_7Mg . IEt_2O + Et_2O$ 5·66 kg. cals.), indicating the existence of a secondary oxonium linkage :



Tertiary amines also catalyse the reaction and presumably form complexes :



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[1] *Compt. rend.*, 1900, **130**, 1322.

[2] *Ber.*, 1905, **38**, 904.

It is evident that isomers may be expected on either Baeyer's or Grignard's formula, the Grignard structural formula, however, is usually adopted, since it indicates more easily the various reactions which may be performed with the reagent

THE FRIEDEL-CRAFTS REACTION

In 1877 Friedel and Crafts[1] showed that anhydrous aluminium chloride was an extraordinarily effective catalytic agent for bringing about condensations of the type

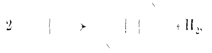
$$C_6H_6 + RX + (AlCl_3) \longrightarrow C_6H_5 - R + HX,$$

where RX is an alkyl halide

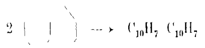
The researches of Jacobsen[2] and of Anschutz[3] have shown that the reaction is reversible Thus, if hydrochloric acid gas be passed into a mixture of toluene and aluminium chloride, benzene may be obtained

Substitution usually proceeds further than the stage indicated above Thus, from benzene and methyl chloride in excess, methylation of the benzene ring can proceed to completion Even when the proportions necessary for the preparation of toluene are taken, the yield is far from theoretical and the product has to be freed by fractionation from the xylenes and mesitylene present

At higher temperatures the aromatic hydrocarbons benzene, or naphthalene will react, undergoing a process of dehydrogenation (see p 283) Thus



and, as shown by Miss Homer,[1] these changes take place much more readily with naphthalene



A similar reaction takes place with the acid chlorides in presence of aluminium chloride, forming ketones,

$$R\ CO\ Cl + (AlCl_3) + C_6H_6 \longrightarrow R\ CO\ C_6H_5 + (AlCl_3) + HCl$$

Utilising carbonyl chloride and subsequently submitting the acid chloride thus formed to hydrolysis, acids may similarly be prepared:

$$COCl_2 + AlCl_3 + C_6H_6 \rightarrow C_6H_5\ COCl \longrightarrow C_6H_5\ COOH$$

The method was extended by Gattermann[5] to the preparation of aldehydes by passing a mixture of dry hydrogen chloride and carbon monoxide into benzene in the presence of aluminium chloride or cuprous chloride:

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[1] *Ber*, 1905 **38** 3661

[2] *Compt rend*, 1877, **84** 1392

[3] *Ber*, 1885, **18**, 339

[4] *Ibid*, 1885, **18**, 657

[5] *Annalen* 1906, **347**, 347

$$C_6H_6 + CO + HCl + (AlCl_3) \dashrightarrow C_6H_5 . CHO + HCl + (AlCl_3).$$

Anhydrous ferric chloride, cuprous chloride, or the finely divided metals such as zinc, copper, aluminium, or amalgamated aluminium have all been suggested as alternative catalytic agents, but, with the exception of cuprous chloride used in Gattermann's reaction, they are all less active than anhydrous aluminium chloride.

The mechanism of the reaction.—In 1901 Perrier isolated from the interaction of aluminium chloride and an acyl chloride in solutions of carbon disulphide crystalline compounds of the formula $R . CO . Cl\ AlCl_3$, whilst a year later Koller showed by cryoscopic measurements that these molecular compounds were complex, having a molecular composition $(R . CO . ClAlCl_3)_2$.

Steele[1] systematically investigated the kinetics of the reaction.

A stream of dry hydrogen was passed through a toluene wash-bottle into a reaction mixture of benzyl chloride and the catalyst (aluminium chloride or ferric chloride), the rate of evolution of hydrochloric acid in the gas stream being measured.

The ratio of catalyst to benzyl chloride was varied within wide limits. It was noted in the preparation of hydrocarbons that there was a small period of induction, the solution becoming of an intense orange colour suggesting the formation of a complex $(C_6H_5 . CH_2Cl . AlCl_3)_2$.

With ferric chloride the period of induction was somewhat longer. The reaction then proceeded uniformly according to a unimolecular law

$$-\frac{dc}{dt} = Kc,$$

until about 25 molecules of hydrochloric acid per molecule of aluminium chloride had been evolved, after which the reaction ceased. It appeared that the primary formation of the complex $(C_6H_5 . CH_3)_2Al_2Cl_6$ took place somewhat rapidly, and that the rate of decomposition actually measured was that of the complex

$$(C_6H_5\ CH_3)C_6H_5 . CH_2ClAlCl_3 \rightleftarrows AlCl_3 + C_{14}H_{14} + HCl.$$

Aluminium chloride is thus a true catalyst, but is removed from the sphere of action by a great excess of the hydrocarbon produced. Ferric chloride requires a still greater excess of hydrocarbon to effect its removal.

Steele's investigations on the catalytic activity of the anhydrous chlorides of aluminium and iron on the condensation of toluene and benzoyl yielded somewhat different results.

With a molecular ratio $AlCl_3 : C_6H_5 . CO . Cl$ varying from 0·65 : 1

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[1] *J. Chem. Soc.*, 1903, **83**, 1470.

o 1 3 1 the evolution of hydrochloric acid was constant for the first en minutes Subsequently it followed the unimolecular law

$$-\frac{dc}{dt} = Kc$$

or a short period and finally ceased

With a ratio 2 3 1 the ratio of decomposition approximates to that of a bimolecular decomposition

$$-\frac{dc}{dt} = Kc^2$$

These results are explicable on the assumption that during the first ten minutes the complex was present in excess of its solubility, *i e* the concentration in the solution of the decomposing complex did not alter for this period, and consequently

$$-\frac{dc}{dt} = K,$$

or the rate of evolution of hydrogen chloride, would be constant Subsequently, in the presence of small amounts of catalyst, decomposition of the complex proceeded in the normal manner, the aluminium chloride being removed molecule for molecule by the reaction product, the ketone $C_6H_5 . CO . CH_2 . C_6H_5$ In the presence of relatively large amounts of aluminium chloride, it must be assumed that the toluene will also form a complex with the catalyst, and that the rate of interaction of two aluminium chloride complexes is being measured

$$(C_6H_5 . CO . Cl . AlCl_3) + (C_6H_5 . CH_3 . AlCl_3)$$

It will be noted that in this case the catalyst is removed molecule for molecule by the reaction products, whilst in the case of hydrocarbon synthesis the catalyst is only removed by a large excess of the product of the reaction Goldschmidt and Larsen[1] showed that the condensation of benzyl chloride and anisol was a reaction of the first order, and confirmed Steele's observation as to the purely catalytic function of the aluminium chloride

That aluminium chloride can form fairly stable complexes with hydrocarbons, as was suggested by Steele, has been shown to be the case by the researches of Gustavin,[2] who has isolated definite compounds such as $C_6H_6 . Al_2Cl_6$

Another application of the catalytic activity of the halides of the elements iron aluminium, and copper is found in the Sandmeyer reaction, in which the halides of copper are utilised to effect the elimination of nitrogen from diazo-compounds, thus

$$C_6H_5 . N_2Cl + Cu_2Cl_2 = C_6H_5Cl + N_2 + Cu_2Cl_2,$$
$$C_6H_5 . N_2Cl + Cu_2Br_2 = C_6H_5Br + N_2 + Cu_2BrCl$$

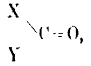
---

[1] *Zeitsch physikal Chem* 1904 **48**, 130

[2] *Compt rend*, 1903, **136** 1065, 1905, **140**, 940

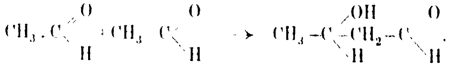
Aldehyde Condensations

The aldol condensation. The condensation of aldehydes and other reactive compounds containing the grouping



$$\begin{array}{l}X\diagdown\\ \qquad C=O,\\ Y\diagup\end{array}$$

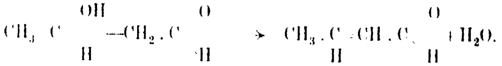
where X and Y are hydrocarbon radicals whilst one may be a hydrogen atom, was first investigated by Wurtz,[1] who showed that acetaldehyde, on standing, slowly polymerised into aldol. This condensation can be catalytically hastened by the addition of small quantities of alkali, such as caustic soda or potassium carbonate, or of acids, such as hydrochloric acid:



$$CH_3.C\begin{smallmatrix}O\\H\end{smallmatrix}+CH_3.C\begin{smallmatrix}O\\H\end{smallmatrix}\rightarrow CH_3-C\begin{smallmatrix}OH\\H\end{smallmatrix}-CH_2-C\begin{smallmatrix}O\\H\end{smallmatrix}.$$

Hydroxybutyraldehyde.

At somewhat more elevated temperatures, and in the presence of certain catalysts, especially dehydrating agents such as sulphuric acid, zinc chloride, or acetic anhydride, the aldol condensation product loses water to form a crotonaldehyde condensation product, thus:

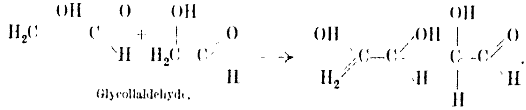


$$CH_3.C\begin{smallmatrix}OH\\H\end{smallmatrix}-CH_2.C\begin{smallmatrix}O\\H\end{smallmatrix}\rightarrow CH_3.\underset{H}{C}=CH.C\begin{smallmatrix}O\\H\end{smallmatrix}+H_2O.$$

Crotonaldehyde.

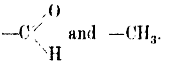
Bakelites, being products of the condensation of formaldehyde and phenols and now extensively used for electrical insulation purposes, are the result of such a series of aldol and crotonaldehyde condensations.

Claisen[2] has made extensive use of dilute caustic soda as catalytic agent in this reaction. Thus, synthesis of erythrose from glycollic aldehyde proceeds smoothly in 10 per cent. caustic soda solution:



$$\underset{\text{Glycollaldehyde.}}{H_2\overset{OH}{C}-\overset{O}{C}\diagdown H}+\overset{OH}{H_2C}-C\begin{smallmatrix}O\\H\end{smallmatrix}\rightarrow \underset{\text{Erythrose.}}{H_2\overset{OH}{C}-C\begin{smallmatrix}OH\\H\end{smallmatrix}-\underset{H}{\overset{OH}{C}}-C\begin{smallmatrix}O\\H\end{smallmatrix}}.$$

Aldehydic and crotonaldehydic condensation may of course continue if the aldol condensation product still contains the groupings



$$-C\begin{smallmatrix}O\\H\end{smallmatrix}\text{ and }-CH_3.$$

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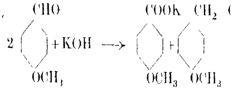
[1] *Compt. rend.*, 1872, **74**, 1361.

[2] *Ber.*, 1881, **14**, 2471.

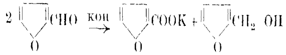
Thus aldehyde resins obtained on boiling acetaldehyde with potash are doubtless of this character Einhorn and Diehl[1] isolated two products of condensation from benzaldehyde and acetaldehyde

$$C_6H_5\ CHO + CH_3\ CHO \longrightarrow C_6H_5\ CH\ CH\ CHO + H_2O,$$
$$C_6H_5\ CH\ CH\ CHO + CH_3\ CHO \rightarrow C_6H_5\ CH\ CH\ CH\ CH\ CHO$$

With the higher aliphatic aldehydes or with the aldehydic grouping attached to an electro-negative cyclic nucleus such as the benzene, pyridine, or furfurane ring, the alkali no longer acts as a simple catalyst but serves as a base, forming, as shown by Cannizzaro, the sodium or potassium salt of the respective acid and the corresponding alcohol, thus



Anisic aldehyde

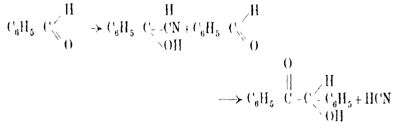


Furfurol

$$(CH_3)_2CH\ CH_2\ CHO \xrightarrow{Ca(OH)_2} \{(CH_3)_2\ CH\ CH_2\ COO\}_2\ Ca$$
$$+ (CH_3)_2CH\ CH_2\ CH_2\ OH$$

Isovaleric aldehyde

The benzoin condensation.- Liebig and Wohler[2] investigated an interesting condensation of benzaldehyde to benzoin, using alcoholic potassium cyanide as catalyst Bredig and Stern[3] studied the kinetics of the process and showed that the cyanide ion was the catalytic agent According to Lapworth[4] an intermediate compound benzaldehyde cyanhydrin, is formed, which subsequently condenses with another molecule of benzaldehyde with the elimination of hydrogen cyanide



Catalytic Changes of Dynamic Isomerides

Many cases of tautomeric changes are influenced by the presence of certain catalytic agents There appears little doubt that on the establishment of a true equilibrium both forms of the tautomeric substance will be present, but in cases of pseudomeric substances (*e.g.* the lactam and lactim forms of isatin) one form is usually practically absent, or present in extremely small quantities This, however, must be attributed to the fact that under the conditions of the experiment the equilibrium has been shifted very far in one direction. Thus, in the usual urea-ammonium cyanate equilibrium, 95 per cent of urea represents the equilibrium amount under normal conditions :

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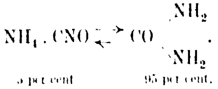
[1] *Ber*, 1885, **18** 2370, Cohen, *Organic Chemistry* p 275

[2] *Annalen*, 1832, **3** 276

[3] *Zeitsch physikal Chem*, 1905, **50**, 513

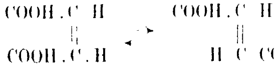
[4] *J Chem Soc* 1903, **83** 995



$$\underset{5\text{ per cent}}{NH_4 . CNO} \rightleftarrows \underset{95\text{ per cent.}}{CO\begin{matrix} NH_2 \\ NH_2 \end{matrix}}$$

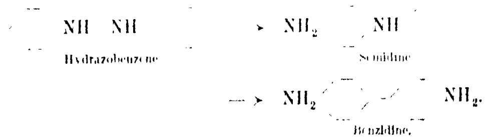
In the case of many allelotropic modifications in which at equilibrium the two forms are present in determinable quantities, each form can be isolated in the pure state and its rate of conversion be determined, provided that the reaction velocity of the re establishment of equilibrium be not extremely rapid.

Much confusion in the past was caused in the classification of types of dynamic isomeric changes owing to the fact that either the intra-convertible forms were extremely labile in the pure state and could frequently not be isolated as such, or, on the other hand, they were very stable and only proceeded to form an equilibrium mixture with difficulty. It is evident that these differences are merely one of degree [1] Lowry has noted that in cases of dynamic isomerism where two radicals are interchanged, and when neither radical can be split off as an ion in either compound, the catalytic agent is invariably an acid or an acidic substance. Thus, in fumaric-maleic acid equilibrium, hydrobromic acid is the most effective catalyst .



$$\begin{matrix} COOH . C . H \\ \| \\ COOH . C . H \end{matrix} \rightleftarrows \begin{matrix} COOH . C . H \\ \| \\ H . C . COOH \end{matrix}$$

In the benzidine conversion mineral acids are invariably used . [2]



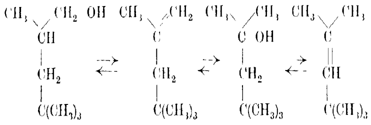
Of historic interest is Butlerow's investigation [3] of the action of trimethyl carbinol in dilute sulphuric acid, a quaternary equilibrium between the two isodibutylenes and their respective alcohols being established

---

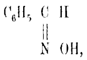
[1] See Lowry, *Brit Assoc. Reports*, 1904, p 193

[2] See Jacobsen, *Annalen*, 1899, **303**, 290, and Goldschmidt, *Ber.*, 1889, **29**, 1369.

[3] *Annalen*, 1877, **189**, 76.

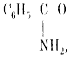


In the Beckmann change,[1] the benzaldoximes,



$$\begin{array}{l} C_6H_5\;C\;H \\ \qquad\;\;\, \| \\ \qquad\;\;\, N\;OH, \end{array}$$

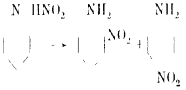
are converted into the acid amides,



$$\begin{array}{l} C_6H_5\;C\;O \\ \qquad\;\;\, | \\ \qquad\;\;\, NH_2, \end{array}$$

by a trace of hydrochloric acid or phosphorus oxychloride

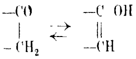
The use of many similar acid catalysts is also to be noticed in the transference of groups from the side chain to the aromatic nucleus Thus, Bamberger[2] obtained the transference of a nitro-group by the addition of a small quantity of mineral acid



Similar transferences of one or more methyl groups have been obtained by Hofmann and Martius,[3] the sulphonic group by Hindermann,[4] as well as the $-NO$ and $-CH_3\,CO$ groupings by different investigators

In those cases in which a single radical is transferred from one position to another and in which the radical may be capable of acting as an ion in both forms or at least in one form, the catalytic agent is, according to Lowry, invariably an alkaline substance

The most important cases of this class of dynamic isomeric change are the keto-enol modifications in which the isomers differ only in the position of a labile hydrogen atom



$$\begin{array}{lcl} -CO & & -C\;OH \\ \;\;\;| & \rightleftarrows & \;\;\;\| \\ -CH_2 & & -CH \end{array}$$

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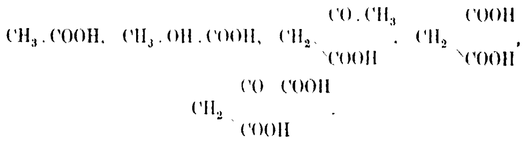
[1] *Ber* 1889, **22**, 1537.

[2] *Ibid*, 1897, **30**, 1288

[3] *Ibid*, 1878, **4**, 742

[4] *Ibid*, 1897, **30**, 654

The reactivity of a hydrogen atom attached to a carbon atom increases as the divergence between the electro-positive and electro-negative groupings in the molecule becomes greater. Thus, in the following compounds the activity or lability of the hydrogen becomes greater owing to the insertion of more electro negative groupings in the molecule :



$$CH_3.COOH,\quad CH_3.OH.COOH,\quad CH_2\begin{array}{l}\diagup CO.CH_3\\ \diagdown COOH\end{array}.\quad CH_2\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array},$$

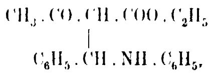
$$CH_2\begin{array}{l}\diagup CO.COOH\\ \diagdown COOH\end{array}.$$

In malonic acid both hydrogens of the nucleus $>CH_2$ have already become labile, and are even capable of replacement by sodium. Aceto-acetic ester has also two labile hydrogen atoms, but only one sodium salt is known.

Acetoacetic ester exists both in the keto and enol forms in solution. Thus, it shows reactivity towards both ketone reagents, such as phenylhydrazine, and to enol reagents, *e.g.* phenylcarbimide or ferric chloride. By the addition of such substances the equilibrium is shifted and complete conversion can finally ensue if sufficient of the reagent be added, although in the case of ferric chloride the complex Fe (enol)$_3$ [$FeCl_3$ + 3 enol form $\rightleftarrows$ Fe (enol)$_3$ + 3HCl] is formed to such a slight extent that the equilibrium is barely affected.

The solvent itself may influence the equilibrium by combining with one or both of the isomeric forms. In these cases also the change from ketonic to enolic form is accelerated by the addition of small quantities of bases.

The work of Schiff on the condensation of acetoacetic ester and benzalaniline[1] has, however, indicated that this catalytic activity of bases in the keto-enol conversion leads to somewhat unexpected results. He noted that complete conversion of the keto form,



$$\begin{array}{c}CH_3.CO.CH.COO.C_2H_5\\ |\\ C_6H_5.CH.NH.C_6H_5,\end{array}$$

to the enol form could be obtained by the addition of a trace of sodium ethoxide to the reagent, whilst the reverse change could likewise be accomplished by the addition of piperidine. Evidently the action is not purely catalytic, since the equilibrium is disturbed ; Lowry has assumed[2] that the sodium ethoxide forms an additive compound with the enol form of acetoacetic ester, which then interacts with the benzaniline and liberates the sodium ethoxide. In this way the enol form of acetoacetic ester is continuously removed from the sphere of action and keto-enol conversion takes place to re-establish equilibrium

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[1] *Ber.*, 1898, **31**, 205 ; 1899, **32**, 332.

[2] *J. Chem. Soc.*, 1899, **75**, 241.

The nitro-bodies. Victor Meyer first indicated the tautomeric nature of nitro-derivatives by isolating methyl nitrite, $CH_3 . O\,NO$ (b p -16°), and nitromethane, CH_3NO_2 (b p 110°), by the interaction of methyl iodide and silver or potassium nitrite Kolbe's experiments on the solubilities of various halogen-substituted nitro-bodies conclusively showed that solubility in alkali was conditioned by the presence of a labile hydrogen atom Thus, all derivatives of the type $>CHNO_2$ were soluble, whilst those of type $-\!\!>CNO_2$ were insoluble

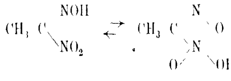
Hantzsch and Schultze,[1] showed that the two isomers in the case of phenyl nitromethane could be transformed one into the other, equilibrium between the two forms being assumed to exist

$$C_6H_5\ CH_2\ NO_2 \rightleftarrows C_6H_5\ CH\ NO\ OH$$

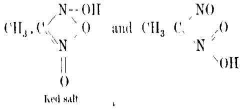
Phenylnitromethane ψ Nitrotoluene

ψ-Nitrotoluene is a strong acid and an electrolyte, whilst phenylnitromethane is an oil and a non-electrolyte The change of the oil into the conducting form is accelerated by the presence of bases, whilst the reverse change is influenced by the addition of acids, in alcoholic solutions also the ψ-nitrotoluene, which can be precipitated in a pure form from its sodium salt, is gradually transformed to the phenylnitromethane form Similar results are obtained with nitromethane Thus, on the addition of baryta water to nitromethane the period of time required for the tautomeric change to complete itself with formation of the barium salt exceeds fifteen minutes

Hantzsch's investigations on these forms of ionic isomerism in pseudo-acids were extended to the nitrolic acids



He was successful in isolating (by neutralisation with caustic soda) the intermediate forms [2]



Red salt

Lowry and E Armstrong[3] and Lowry[4] have followed the tautomeric changes of the isomeric nitro- and π-bromonitrocamphor by means of the change in optical rotatory power. The normal form of π-bromonitrocamphor,

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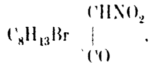
[1] *Ber*, 1896, **29**, 699, 1899 **32** 575

[2] See also Hantzsch's investigations on ψ ammonium bases, *Ber*, 1899 **32**, 594, 1900, **33**, 278

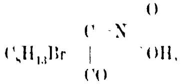
[3] *J Chem Soc*, 1903, **83**, 1314

[4] *Ibid*, 1899 **75** 235



$$C_8H_{13}Br\begin{array}{l} CHNO_2 \\ \quad | \\ CO \end{array}$$

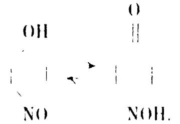
has a rotatory power $[\alpha]_D - 51°$, whilst the *ψ* form,



$$C_8H_{13}Br\begin{array}{l} C=N\begin{array}{l} O \\ \\ OH, \end{array} \\ \quad | \\ CO \end{array}$$

has a value $[\alpha]_D + 188°$.

Similar tautomeric changes are observed in the case of nitrophenol and quinonemonoxime :



A well-investigated case of catalytic influence on the migration of an atom within the molecule is to be found in the catalytic conversion of acetochloroaniline to *p*-chloroacetanilide :

$$C_6H_5 . NCl(CO . CH_3) \rightarrow ClC_6H_4 . NH(CO . CH_3)$$

The reaction is of importance in the consideration of the question of reactivity of various agents with anilines and anilides. Blanksma[1] measured the velocity with which this change occurs in presence of hydrochloric acid, and showed that the reaction was apparently unimolecular but that by doubling the acid concentration the velocity constant of the reaction was increased fourfold. With sulphuric acid it was impossible to obtain constancy in the velocity determinations. Light was shown to possess a marked accelerating action.

Orton[2] and Orton and Jones[3] showed in the course of experiments on the interaction of various acids with chloroamines that chlorine could always be detected when hydrochloric acid was present, but not when one of the other acids was present. This fact led, on further investigation, to the conclusion that the reaction proceeded in two stages :

$$(1) \quad C_6H_5NClAc + HCl \rightleftarrows C_6H_5NHAc + Cl_2,$$
$$(2) \quad C_6H_5NHAc + Cl_2 \rightarrow C_6H_4ClNHAc + HCl,$$

the first reaction proceeding slowly whilst the second reaction proceeded with great speed.

The reaction, therefore, would be proportional to the concentration of the acetochloroanilide and consequently of the first order as found by Blanksma.

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[1] *Proc. K. Akad. Wetensch. Amsterdam*, 1902, **5**, 178, 359.

[2] *Proc. Roy. Soc.*, 1902, **71**, 156.

[3] *J. Chem. Soc.*, 1909, **95**, 1456.

Acree and Johnson[1] assume, in explanation of the reaction mechanism, that a compound between the acetochloroamine and hydrochloric acid is formed which is dissociated, the undissociated fraction, however, being slowly changed over into *p*-chloroacetanilide with simultaneous liberation of free hydrochloric acid.

Rivett[2] suggested that the undissociated hydrochloric acid molecule plays the principal part in the formation of the intermediate compound and that the ions exert an accelerating influence on the reaction. Rivett further investigated the action of neutral chlorides on the change in presence of hydrochloric acid. The usual accelerating influence of neutral salts was observed, and could be stated in the form of an equation of the form

$$K = (HCl)\{0.050 + a(H) + b(Cl') + d(M')\},$$

where *a*, *b*, and *d* are specific constants, dependent only on the nature of the particular ions present. Ammonium chloride constituted an exceptional case, the reaction at the outset in presence of varying quantities of salt going much more slowly, at the end, however, with much greater rapidity than in the pure acid alone.

Harned and Seltz[3] showed that the "neutral salt" action observed was in agreement with values anticipated from the effect of the neutral salts on the activities of the reacting ions. They found that the reaction velocity could be defined over wide variations in concentration by the relationship

$$\frac{dx}{dt} = Kc_1c_2c_3f_2f_3$$

where c_1 is the concentration of the chloroacetanilide, c_2f_2, c_3f_3 the concentrations and activity coefficients of the hydrogen and chlorine ions in the solution.

The cyanides. Attention may be directed to the somewhat complex case of the cyanide-isocyanide tautomeric substances. It is well known that the production of either cyanide or isocyanide can be controlled by utilising the potassium or silver salt of hydrocyanic acid for interaction with an alkyl iodide, thus

$$\begin{array}{ll} & KCN \longrightarrow CH_3\cdot CN \\ CH_3I & \\ & AgCN \longrightarrow CH_3\cdot NC \end{array}$$

We may assume that the alkyl cyanides and isocyanides themselves are tautomeric and that the production of cyanide by the use of the potassium salt is due to the necessity of heating the reacting substances, KCN and CH_3I, to a higher temperature than for the silver salt.[4] It seems probable, however, that the difference in the two reactions is more fundamental.

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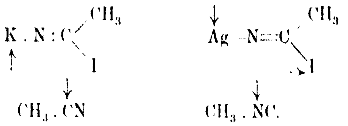
[1] *Amer. Chem. J.*, 1907, **38**, 265.

[2] *Zeitsch. physikal. Chem.*, 1913, **82**, 201; *ibid.*, 1913, **85**, 113.

[3] *J. Amer. Chem. Soc.*, 1922, **44**, 1484.

[4] Wade, *J. Chem. Soc.*, 1902, **81**, 603.

Hydrocyanic acid itself probably possesses the structure H . C N, since it is easily hydrolysed by alkalis, and both in refractive power and physiological activity is more akin to the alkyl cyanides. All the metallic cyanides, however, resemble the alkyl isocyanides both in their reactivity to form double compounds and in their physiological effects. Thus, we must regard the constitution of both silver and potassium salts as similar and of the form K . N C and AgN C. With Nef we may regard the formation of cyanide and isocyanides as determined by the influence of the difference in the electrical character of the metallic ion and the formation of the salts to take place through the mechanism of additive products :



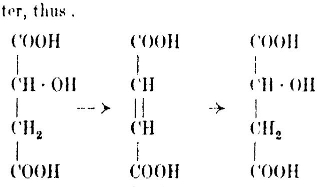
Thus potassium must be regarded as more electro-positive than both CH_3 and CH_3I, whilst silver on this view is comparable with CH_3.

The elements potassium and silver, in the ionic form, consequently exert selective action on account of their differences in electrical characteristics.

RACEMISATION AND MUTAROTATION

Racemisation. In several well-known examples of racemisation of optically active forms of compounds certain catalysts accelerate the conversion and are frequently utilised instead of the more usual method of elevating the temperature ; thus, although active tartaric acid when heated to 170° *per se* is converted into the racemic and meso forms, conversion into the racemic form can be produced at a lower temperature by the addition of aluminium oxide.

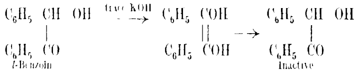
Active malic acid is racemised by heating to 101° with water. These changes are generally attributed to the elimination and subsequent addition of water, thus :



Active malic. Inactive fumaric. Inactive malic

Leucine (α-amidocaproic acid) and hyoscyamine are particularly sensitive to the presence of small quantities of hydroxyl ions, and the latter compound has been utilised for measuring the strength of bases by following polarimetrically the rate of racemisation.[1]

A similar result was obtained by Wren[2] in the racemisation of *l*-benzoin by means of a trace of caustic potash. He was successful in isolating the intermediary enol form.



$$\begin{array}{c} C_6H_5\ CH\ OH \\ | \\ C_6H_5\ CO \end{array} \xrightarrow{\text{trace KOH}} \begin{array}{c} C_6H_5\ COH \\ \| \\ C_6H_5\ COH \end{array} \longrightarrow \begin{array}{c} C_6H_5\ CH\ OH \\ | \\ C_6H_5\ CO \end{array}$$

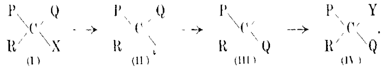
l-Benzoin Inactive

In the examples cited above attention has been directed to the catalytic activity of traces of alkali, and its activity has been attributed to the formation of unstable intermediary compounds without any stress being laid on the function of the alkali during the process of optical inversion.

In the case of the so-called Walden inversion, however, where the catalyst functions in the chemical reaction itself and not purely in a catalytic capacity, the magnitude and nature of the optical inversion is not independent of the nature of the added catalyst and chemical reactant but is greatly influenced by it.

The Walden inversion. The Walden inversion was first observed in α-hydroxy acids of the type R[C]HOH COOH, and various suggestions were advanced in which an essential part of the mechanism was assigned to the H, OH, CO, or even to two of these radicals. Since, however, Pickard and Kenyon[3] have noted inversion in secondary alcohols, *e g* C_6H_{13}[C]HOH CH_3, and Philips[4] Kenyon, and Turley[5] obtained inversion in the conversion of compounds of the type XHRC OP → XHRC OQ, it is clear that neither the carboxyl group nor the α-hydrogen plays an essential part in the mechanism of inversion accompanying the change OH → Br → OH or OH → Cl → OH.

Fischer,[6] Werner[7] and Pfeiffer[8] supposed that the radicals could push one another on the surface of a sphere of affinity with the result that optical inversion may be brought about by the interchange of two radicals, *e g*



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[1] Bredig and Wall *Ber* 1888 **21** 2777

[2] *J Chem Soc*, 1909, **95** 1583

[3] *J Chem Soc*, 1911, **99**, 45

[4] *J Chem Soc* 1923, **123**, 44

[5] *Ibid* 1924 **125** 399

[6] *Annalen* 1911 **381** 132

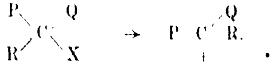
[7] *Ber*, 1911, **44**, 881

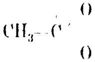
[8] *Annalen*, 1911, **383**, 123

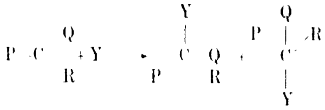
It is clear that only one radical, Q, in addition to X and Y, is involved in the change according to this view.

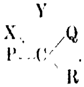
Lowry, following Gadamer,[1] suggests that optical inversion depends on the flattening of the group (II) when X is resumed, followed by a restoration of the tetrahedral configuration when Y is added to the other side of this residue. It is assumed that the Walden inversion is limited to an exchange of anions, the asymmetric carbon atom assuming momentarily the form of a cation.

According to this view the process may be regarded as pursuing the following stages:



The planar ion {CPQR} is comparable to the ion NO_3, CO_3, or  in basic beryllium acetate.[2] If the ion becomes free the anion Y may be added to either side, and thus racemisation results:



If, on the other hand, new negative radicals X and Y are added to opposite sides of the planar ion simultaneously, X then leaving the complex CPQRYX, the compound CPQRY will be formed, when a change in configuration corresponding to a Walden inversion takes place. Finally, the two negative radicals X and Y may be added to the same side of the planar ion simultaneously forming a complex, .

When X leaves the complex a normal substitution of Y for X will have taken place.

Mutarotation.—Very similar to these changes in optical activity on the addition of certain catalysts to organic substances containing an asymmetric carbon atom in juxtaposition to an electro-negative grouping such as the carboxyl group, is the behaviour of certain sugars on standing in aqueous solution or in a slightly alkaline medium.

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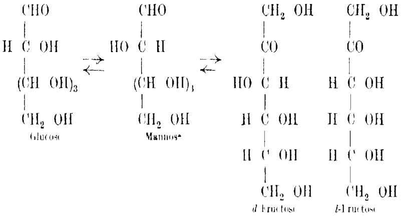
[1] *Chem. Zeit.*, 1912, **36**, 1327.

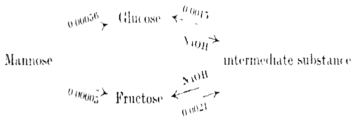
[2] Bragg and Morgan, *Proc. Roy. Soc.*, 1923, **104**, 437

Parcus and Tollens[1] tabulated the initial and final specific rotations of the solutions of a number of natural sugars after being allowed to stand in an alkaline solution for some hours For example, *d*-glucose $\alpha_D + 105\ 2^{\circ}$ sinks to $\alpha_D + 52\ 6^{\circ}$ after a few hours and remains constant at that figure Xylose $\alpha_D + 78\ 6^{\circ}$ sinks to $\alpha_D + 19\ 2^{\circ}$, and rhamnose $\alpha_D - 3{\cdot}0^{\circ}$ rises to $\alpha_D + 9\ 1^{\circ}$

Lobry de Bruyn[2] and V Ekenstein[3] noted the interconversion of glucose, mannose, and fructose on the addition of a little alkali to one of the sugars



Morrel and Bellars[4] obtained similar results with guanidine, which is nearly as strong a base as caustic soda, but has the advantage of forming crystalline compounds with the sugars which may thus be isolated These investigators obtained the following values of the velocity coefficients of each change at 37°



Tanret[5] isolated three modifications of glucose itself α-glucose crystallised from cold solutions, $\alpha_D + 105^{\circ}$, β-glucose from hot solutions, $\alpha_D + 52\ 5^{\circ}$, and γ-glucose from hot alcohol, $\alpha_D + 22\ 0^{\circ}$ β-Glucose is in all probability a dynamic isomer of the other varieties

Both the formation of isomeric glucoses and the conversion of glucose into isomeric sugars may be attributed to the addition of water followed by subsequent dehydration

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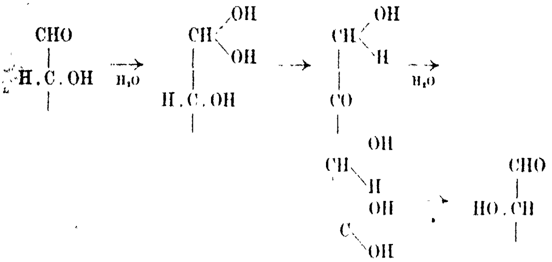
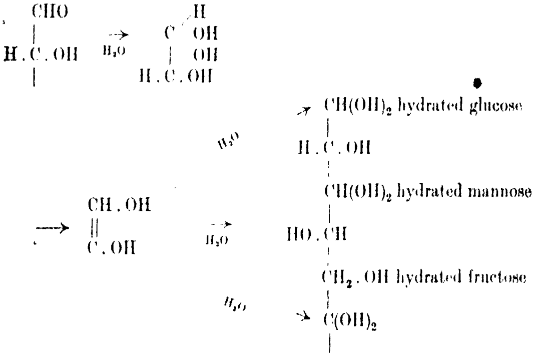
[1] *Annalen*, 1890, **287**, 160. [2] *Rec trav chim*, 1900 **17**, 1 [3] *Ber*, 1895, **28**, 3078
[4] *J Chem Soc*, 1907, **91**, 1010 [5] *Compt rend*, 1895, **120**, 1860

The interconversion of glucose to mannose and fructose may be interpreted thus :



Lowry[1] suggests an alternative scheme in which the hydrated glucose loses water to form an enolic compound from which all the sugars may be derived :



The mutarotation is catalysed both by hydrogen as well as by hydroxyl ions, the velocity constant being expressible in the form

$$K = \cdot 0096 + 0 \cdot 258[\dot{H}] + 9750[OH']$$,

from the measurements of Hudson.[2]

As originally suggested by Euler,[3] we may regard glucose as an amphoteric substance possessing both acid K_a and basic K_b dissociation constants In aqueous solutions at the isoelectric point defined by

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[1] *Loc. cit.*, 1314.

[2] *J. Amer. Chem. Soc.*, 1907, **29**, 1572; *Zeitsch. physikal. Chem.*, 1903, **49**, 487; *J. Amer. Chem. Soc.*, 1917, **39**, 370; *ibid.*, 1919, **41**, 557.

[3] *Zeitsch. physikal. Chem.*, 1901, **36**, 681.

$$C_H = \sqrt{\frac{K_a}{K_b} K_w},$$

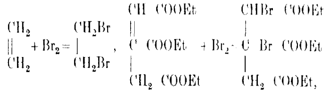
where K_w is the dissociation constant of water, the reaction velocity of mutarotation will be a minimum This minimum is found to be at $P_H = 5·0$ at 5·2° C, and since the direct determination of the dissociation of the sodium glucosate yielded a value of K_a at 5·2° C $= 2·1 \cdot 10^{-13}$, we find that the basic dissociation constant of glucose has a value of $K_b = 4·8 \cdot 10^{-18}$ The reaction velocity constant can accordingly be expressed in the form

$$K = K_0 + r\frac{K_b}{K_w}[H] + r_1\frac{K_a}{[H]},$$

where r and r_1 are the specific reactivities of the glucose cation and anion, and K_0 the reaction constant of the amphoteric glucose "zwitter ion"

HALOGENATION

Several catalytic agents are employed for introducing the halogens into organic compounds, of which the most in[illegible]esting is [illegible] direct sunlight or exposure to various forms [illegible] radiant ene[illegible] action of bright sunlight on the halogenation of unsat[illegible] carbons favours the formation of simple additive prod[illegible] bromination of ethylene or of aconitic ester



$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + Br_2 = \begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array}, \quad \begin{array}{l} CH\ COOEt \\ \| \\ C\ COOEt \\ | \\ CH_2\ COOEt \end{array} + Br_2 = \begin{array}{l} CHBr\ COOEt \\ | \\ C\ Br\ COOEt \\ | \\ CH_2\ COOEt, \end{array}$$

or in the chlorination of benzene

$$C_6H_6 + 3Cl_2 = C_6H_6Cl_6,$$

in which hexachlorohexamethylene is formed, but which is unstable and rearranges according to the equation

$$C_6H_6Cl_6 = C_6H_3Cl_3 + 3HCl$$

In the dark, s[illegible] substitution of a halogen atom for a hydrogen atom usually results

In the case of the [illegible] fatty aromatic hydrocarbons and their derivatives, direct sunlight favours the halogenation of the side chain and not the nucleus, a similar result be[illegible]ng obtained when the process is conducted at the boiling point. Substitution in the nucleus results from halogenation in the dark, as exemplified in the following reactions:

$$C_6H_5.C_2H_5 \begin{array}{l} \nearrow C_6H_5.CHBr.CH_3 \text{ in diffused sunlight} \\ \searrow C_6H_5.CHBr.CH_2Br \text{ in bright sunlight.} \end{array}$$

Several elements or their anhydrous chlorides, the latter frequently formed *in situ*, likewise accelerate the process of halogenation to a marked degree.

Iodine has been successfully employed for processes of chlorination and of bromination.[1] Substitution in the nucleus usually results when iodine is used as catalyst in the halogenation of aromatic substances. Its function as a halogen carrier is probably dependent on two factors—first, the formation of a monohalide, for example ICl or IBr, which in virtue of its unsymmetrical character, as opposed to Cl . Cl or Br . Br, is capable of reacting with unsaturated linkages: secondly, the power of oscillation of the halides of iodine between the two stages of halogenation,

$$ICl + Cl_2 \rightleftharpoons ICl_3,$$

thus exhibiting a marked case of carrier action. In a later chapter on the action of radiant energy in promoting chemical change the further action of iodine in removing the negative catalyst, oxygen, from a system undergoing halogenation is emphasised.

Various varieties of charcoal[2] rapidly effect the combination of hydrogen and chlorine. During the last few years wood charcoal has been employed, as suggested by Schiel,[3] in the preparation of the poison gas, carbonyl chloride, from chlorine and carbon monoxide. In this synthesis it is interesting to note that hydrogen chloride is said to be a negative catalyst, and the preparation of dry carbon monoxide on a large scale offered at first considerable technical difficulties, which were finally overcome by burning charcoal in oxygen and diluting the gas with carbon dioxide in order to prevent undue elevation of the temperature. Ethyl chloride also can be progressively and quantitatively converted into hexachloroethane by chlorination at 350° in presence of blood charcoal.

Sulphur and sulphur chloride have been employed as catalysts for the chlorination of acetic acid to yield the monochloro-derivative.[4]

Phosphorus pentachloride generally undergoes partial or complete conversion to the oxychloride when present in the chlorination of aldehydes and ketones.

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[1] Muller, *Jahresber. Ges. vaterl. Kultur*, 1862, p. 414; Kraft, *Ber.*, 1877, **10**, 801; Klasson, *ibid.*, 1887, **20**, 2382; Bruner and Dluska, *Bull. Acad. Sci. Cracow*, 1907, p. 691.

[2] Paterno, *Gazzetta*, 1878, **8**, 233.

[3] *Jahresber. Ges. vaterl. Kultur*, 1864, p. 309.

[4] Auger and Behal, *Bull. Soc. Chim.*, 1889, **2**, 145; Russanoff, *Ber.*, 1892, **25**, 334.

in the effect of acids on the organic nitro-compounds, in the keto-enol isomeric substances, and also in the conversion of unsaturated acids into $\alpha\beta$-derivatives in the presence of acids, *e.g.*

$$CH_3\,CH_2\,CH\,CH\,CH_2\,COOH \dashrightarrow CH_3\,CH_2\,CH_2\,CH\,\overset{(x)}{CH}\,COOH,$$

the tendency in this case being to increase the reactivity or labile nature of the last hydrogen atom (x), which, as we have noted in the case of atomic groupings of high reactivity, may react with caustic soda or sodium ethoxide to form a

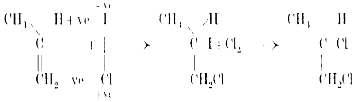
$$CNa\;COOH$$

derivative. In the cases of conversion of $\beta\gamma$- and some $\gamma\delta$- unsaturated acids into the $\alpha\beta$-derivatives, no secondary reaction of this nature does in fact take place, since the reactivity of the labile hydrogen is never sufficiently great. The caustic soda is thus a purely catalytic agent.

The same phenomenon can be noted in the case of butyl acetylene, $(CH_3)_2C\;C\;CH$, which, when gently warmed, passes into dimethyl allylene, $(CH_3)_2C\;C\;CH_2$, whilst on treatment with metallic sodium the reverse change takes place.

The catalytic activity of a trace of iodine in the addition of chlorine to an unsaturated compound is readily intelligible from this point of view. It is at first sight difficult to see why I Cl should be more reactive than Cl Cl, since the formation of the iodochloride is itself an exothermic reaction.

The relative differences in the electro-positive and electro-negative nature of the couplet Cl I, however, compensate for the loss of energy and permit of a relatively higher reactivity.



It would appear that the stability of any organic compound is dependent on its electronic character and its symmetry. Additive agents only exert a catalytic activity when there is a tendency to salt formation due to the above considerations; thus, the problem resolves itself into a formulation of the intermediate compound theory in which the stability of the intermediate compounds is governed by electronic forces.

The inherent difficulty in the development of this theory to explain both organic chemical reactions in general and catalytic action in particular lies in the fact that we have no means of measurement of the electro-positive or -negative nature of an atom or a grouping of atoms within a molecule; we can merely state that halogens and acid radicals are opposite in character to the hydrogen atom and hydrocarbon radicals, whilst increasing unsaturation increases the acid or electro-negative character of a hydrocarbon nucleus. The measurement must naturally include two factors, the absolute value and the effect of spatial arrangement on the electronic nature of neighbouring atoms.

CHAPTER XV

CATALYSIS IN ELECTRO-CHEMISTRY

CATHODIC REDUCTION

ELSEWHERE in this book we have noted the various applications of catalytic substances to accelerate the reduction of certain compounds in liquid media by means of gaseous hydrogen. With the aid of the electric current we have a means at hand of generating hydrogen *in situ* and can thus accomplish similar processes of reduction. In spite of the higher cost of hydrogen produced in this way, processes of electrolytic reduction are becoming increasingly important not only on account of the greater cleanliness of the operations, but also owing to the variety of products which can be obtained by a strict control of the reducing power of the hydrogen. It is in this strict control over the reducing power that the great merit of electrolytic processes lies.

During the course of electrolytic reduction, two catalytic reactions are to be observed—first, the specific action of the cathode material on the course of reaction; and secondly, the effect of adding certain salts to the electrolyte in which reduction is proceeding. These two actions are frequently entirely distinct from one another, but in many cases mutual interference is so marked that distinction between phenomena occurring in the electrolyte and at the electrode surface is impossible.

The specific action of the electrode material.—Since, in electrolytic reduction, the hydrogen is produced at the surface of the cathode exposed to the electrolyte, we should expect that the course of the reactions proceeding in the adherent film would affect the nature of products obtained by reduction. This is actually found to be the case. Thus, in the electrolytic reduction of nitrobenzene, the quantity of the various products of reduction, nitrosobenzene, phenylhydroxylamine, amido-phenol, azoxybenzene, hydrazobenzene, benzidine, azobenzene, and aniline, can be controlled at will by an alteration in the electrode reactions.

The primary electrode reaction, occurring at the cathode in the electrolysis of a dilute acid, is the discharge of hydrogen ions with the liberation of molecular hydrogen:

$$2H^{\cdot} \longrightarrow 2H + 2\epsilon \longrightarrow \overset{\uparrow}{H_2}.$$

When the molecular hydrogen evolved and the hydrogen ions in solution are in dynamic equilibrium, as found in an oxygen-hydrogen cell with perfectly reversible electrodes, the cathodic potential of the electrode in the electrolyte is given by the general formula developed by Nernst:

$$E = \frac{RT}{2F}\log_e\frac{H_2}{\dot{H}},$$

where F is the Faraday equivalent (96,540 coulombs per gram molecule), n the valency of the discharged ion (in this case $n = 1$), H_2 and $\dot{H}$ the partial pressure and the ionic concentration of the hydrogen gas and the hydrion in solution respectively.

It follows that for the steady liberation of cathodic hydrogen from an electrolyte of unchanging composition a minimum potential difference between cathode and electrolyte must be applied, which cathodic potential has an important influence on the reducing power of the electrolytic hydrogen.

The investigations of Caspari,[1] Müller,[2] J. Tafel,[3] and Wilsmore[4] have shown that the value of E, the cathode potential derived from Nernst's formula, is not independent of the nature of the electrode material, as is assumed when conditions of dynamic equilibrium between the molecular, atomic, and ionic hydrogen at or in the electrode surface are postulated. Such conditions of reversibility are only obtained when platinised platinum is used as cathode material and very low current densities are employed. All other metals give values for the cathode potential in excess of the calculated value for E. In the following table are given the magnitudes of this excess or over-potential (η) required to effect the liberation of molecular hydrogen at various metal surfaces:

Metal.	Over potential in Volt	Metal	Over-potential in Volt.
Hg	0·78	Ni	0·21
Zn	0·70	Ag	0·15
Pb	0·64	Pt (bright)	0·09
Sn	0·53	Fe	0·08
Cd	0·48	Au	0·02
Pd	0·46	Pt (platinised)	0·005
Cu	0·23		

Thus the transformation of hydrion into molecular hydrogen requires $\frac{E+\eta}{E}$ times as much energy as is necessary at a perfectly reversible electrode Eventually this excess energy reappears in the electrolyte as additional heat, since no subsidiary endothermic reactions have taken place

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[1] *Zeitsch. physikal. Chem.*, 1899, **92**, 30.

[2] *Zeitsch. anorg. Chem.*, 1900, **1**, 26.

[3] *Zeitsch. physikal. Chem.*, 1905, **50**, 641.

[4] *Ibid.*, 1900, **35**, 291.

It is evident that the various metals exert marked catalytic activity in the transformation of ionic into molecular hydrogen

$$2\dot{H} \longrightarrow 2H \longrightarrow H_2$$

Whilst the original suggestion of Helmholtz[1] that over-potential was caused by the presence of small bubbles present on the electrode surface has received support from investigators such as Moller[2] and MacInnes and Adler,[3] it has been shown in numerous investigations that whilst the formation of bubbles which affect the current density by covering up part of the electrode electrolyte interface may cause slight fluctuations in the over-potential, the phenomenon itself is due to the pressure of some electromotively active form of hydrogen in the electrode According to Newbery,[4] Glasstone,[5] and others this electromotively active form of hydrogen is present in the electrode as a chemical compound in the form of a hydride of definite chemical composition It is, however, questionable whether these hydrides do actually exist, and even if they were present whether their properties would be such as to be electromotively active with a virtual solution pressure greater than for gaseous hydrogen It is more than probable, as Tafel pointed out,[6] that, on the discharge of hydrions, the hydrogen atoms subsequently react to form hydrogen molecules on the surface If the metal exerts a marked catalytic activity for the surface recombination of hydrogen atoms, the concentration of atoms on the surface will at all times be low Thus the over-potential, which is a measure of the concentration of the electromotively hydrogen atoms on the surface, will be small for metals (catalytically active) in promoting the union

$$2H \rightarrow H_2$$

This view in several modified forms has been supported by the experiments and considerations of Bancroft,[7] Bennet and Thompson,[8] Rideal[9] and Westrip,[10] and others[11] Metals with high over-voltages will possess a high surface concentration of bound hydrogen atoms when current is flowing They will have only a small tendency to dissociate hydrogen molecules and will thus exert but a small catalytic activity for hydrogenation processes in which the activation of the hydrogen is necessary

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[1] *Theorie der Warme*, p 309

[2] *Zeitsch physikal Chem* 1909 **65** 226

[3] *J Amer Chem Soc* 1919 **41**, 194, 1920 **42** 194

[4] *J Chem Soc* 1916 **109** 1051 1359, 1922 **121** 7 *J Amer Chem Soc* 1920, **42** 2007 *Trans Farad Soc*, 1919, **15**, 126

[5] *Ibid* 1923, **123**, 1745, 2926

[6] *Zeitsch physikal Chem*, 1900 **34** 200

[7] *J Physical Chem* 1916 **20**, 396

[8] *Ibid* 1916, **20**, 296

[9] *J Amer Chem Soc*, 1920, **42** 94

[10] *J Chem Soc*, 1924 **125** 1112

[11] Bonhoeffer, *Zeitsch physikal Chem*, 1924, **113**, 199

If θ be the surface concentration of adsorbed hydrogen atoms, the rate of formation of molecular hydrogen from the atoms will be

$$-\frac{dx}{dt} = K\theta^2$$

The rate of formation of hydrogen atoms on the surface will be proportional to the current density, or $= K'i$ where i is the current.

When equilibrium is established,

$$K\theta^2 = K'i$$

or

$$\theta = \sqrt{\frac{K'}{K}i}$$

The over-voltage η is according to this conception defined by the surface concentration of adsorbed monatomic hydrogen, or

$$\eta = \frac{RT}{F}\log\frac{C_H\theta}{C_H},$$

where C_H is the electrolytic solution pressure of the monatomic adsorbed hydrogen, whence

$$\eta = \frac{RT}{F}\log\frac{C_H}{C_H}\sqrt{\frac{K'}{K}i} = a + \frac{RT}{2F}\log i$$

in a solution of constant hydrion concentration and constant electrode electrolyte interface. This equation has been fully established by Tafel.[1]

It would prove of interest to measure the rate of decay of the hydrogen over-potential with the time in order to obtain a measure of the catalytic efficiency of the various metals, for Bonhoeffer[1] has shown that in the case of the catalytic decomposition of gaseous atomic hydrogen the catalytic efficiencies of various metals are in the order anticipated from this hypothesis as to the origin of the over-potential.

According to the measurements of Knobel, Caplan, and Eiseman,[2] the limiting value for the over-voltages of all metals except gold, silver, and platinum is 1·3 volts at high current densities. It is possible that under these conditions $\theta = 1$, whence

$$\eta = \frac{RT}{F}\log\frac{C_H}{C_H} = 1\cdot3 \text{ volts},$$

giving a value of 30,000 cals. per grm.-atom for the free energy of the adsorbed hydrogen atoms in excess of the ordinary hydrogen electrode datum as standard.

The work of Haber[3] has indicated that the cathode potential is the determining factor in the reducing power of electrolytic hydrogen.[1] By careful adjustment of this value he was able to isolate a great variety of compounds by the simple reduction of nitrobenzene in acid and alkaline electrolytes, according to the following scheme

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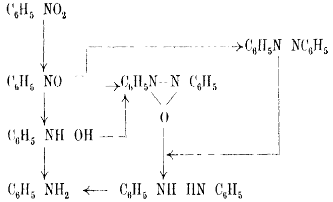
[1] *Loc. cit.* p. 214.

[2] *Trans. Amer. Elektrochem. Soc.*, 1923, **43**, 55.

[3] *Zeitsch. Elektrochem.*, 1898, **4**, 506; *Zeitsch. physikal. Chem.*, 1900, **32**, 173, 271, and 1904, **47**, 263.



Utilising a 2 per cent caustic soda solution as electrolyte, Lob and Moore obtained the following results

Electrode Material	Over-voltage Value	Product
Pt, Ni	0 15 0 23	Azoxybenzene
Pb, Sn, Zn	0 64, 0 53, 0 70	Azobenzene
Cu	0 46	Aniline

The production of aniline, however, proceeds most rapidly in an acid electrolyte using a lead[2] or zinc cathode[3]

The effect of agents added to the electrolyte - It will be noted that the catalytic activity of copper in the reduction of nitrobenzene to aniline is somewhat anomalous in view of its relatively small over-potential

This point was investigated in detail by Chilesoti and Tafel,[4] who noted that metallic copper itself could rapidly effect the reduction of phenylhydroxylamine to aniline with the formation of cupric ions in solution Thus, the copper electrode is functioning as a reducing agent, not only by reason of the liberation of hydrogen at the surface but by actual solution and re-deposition of the metal

$$Cu + 2\ominus \rightleftarrows Cu^{\cdot\cdot}$$

If ferrous salts be added to the electrolyte, a similar catalytic activity is noticed[5] Thus, ferrous ions are oxidised to ferric ions by reduction of the phenylhydroxylamine, whilst the ferric ions thus formed are reduced at the cathode surface. In those cases where the cathodic potential is not sufficiently high to deposit the ions of the added salt, it is evident that unless precautions be taken to separate catholyte from anolyte a carrier action between anode and cathode may occur by which current may flow by means of the alternate oxidation and reduction of the polyvalent ion, thus:

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[1] See also H Goldschmidt, *Zeitsch Elektrochem*, 1900, **7**, 263, Nernst, *Zeitsch physikal Chem* 1904, **47**, 52, and Brunner, *ibid* 56

[2] Lob *Zeitsch Elektrochem* 1898, **4**, 430

[3] Elbs, *Chem Zeit*, 1893, **17**, 209

[4] *Zeitsch Elektrochem*, 1901, **7**, 768, *Zeitsch anorg Chem*, 1902, **21**, 289

[5] Farnau, *J Physical Chem.*, 1912, **16**, 249

$$\mathrm{Fe}^{\cdot\cdot} + \oplus \rightleftarrows \mathrm{Fe}^{\cdot\cdot\cdot}.$$

This species of carrier action is frequently observed in electro-chemical processes, *e.g.* the presence of 0·1 per cent of ferric salt, a very common impurity, in carnallite is sufficient to reduce the current efficiency in the production of magnesium by more than 20 per cent. Carrier action is also frequently made use of in the electrolytic deposition of metals when divided cells are employed for electrolysis.

In the electro-deposition of copper, ferric sulphate is frequently employed as a leaching agent for roasted copper ores. A solution of cuprous and ferrous sulphate is thus formed from which copper is deposited in the cathode compartment of a cell, the spent liquor containing ferrous sulphate being returned through the anode compartment, where it is reoxidised to the ferric state preliminary to the treatment of a fresh batch of ore.

Tafel's experiments[1] on the electrolytic reduction of nitric acid to ammonia at lead and copper cathodes also indicate that copper exerts an anomalously high reactivity; in this case electrolytic reduction of nitric acid proceeds as far as hydroxylamine, whilst the second stage in the reduction process is performed almost *entirely by the carrier* action of the copper, $\mathrm{Cu}^{\cdot\cdot} \rightleftarrows \mathrm{Cu} + 2\ominus$. *A number of processes have* been devised for accelerating the process of electrolytic reduction *by* these *means, primarily using suitable cathode material to obtain the* requisite cathode potential, and secondarily to promote the carrier action between electrode and electrolyte by the addition of metallic powder or salts of polyvalent elements.

For example, copper or tin is used in the electrolytic reduction of *o*- or *p*-nitrotoluene to *o*- or *p*-toluidine,[2] zinc in the preparation of hyposulphites,[3] mercury, vanadium, iron, or titanium in the electrolytic reduction of indigo, titanium being frequently used in the reduction of quinone to hydroquinone. In addition to the phenomenon of hydrogen over-voltage at the electrode and the possibility of ionic carrier action by partial solution and re-precipitation of the metallic electrode, the metal itself may exert a specific catalytic effect in the reduction process. It is reasonable to assume that, since various metals exert a catalytic influence on the rate of combination of the discharged hydrogen, they may also affect the alternative reaction between the atomic hydrogen and the depolariser

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[1] *Loc. cit.*

[2] D.R.P. 117007/1900.

[3] See Jellinek, *Zeitsch. Elektrochem.*, 1911, **17**, 157, and D.R.P. 139567/1902.

Thus, the reduction of chlorates to chlorides proceeds smoothly at an iron cathode, which is superior to platinised platinum in this respect We may regard the catalytic activity of the iron to be evident in both the cathodic processes

(*a*) The combination of atomic hydrogen to the molecular state .

$$2H \rightarrow H_2$$

(*b*) The reduction of the chlorate ion by the atomic hydrogen

$$2H + ClO'_3 \longrightarrow ClO'_2 + H_2OClO'_2 + 2H \rightarrow ClO' \cdot \rightarrow Cl'$$

In this case the second process, the reduction of the chlorate, is accelerated by the iron, whilst, as shown by the over-potential value, the acceleration of the production of molecular hydrogen is distinctly inferior to that of platinised platinum

The addition of colloidal materials to simple electrolytes as well as the use of complex electrolytes has marked effects on the nature of deposited metals and alloys, a discussion, however, of the mechanism by which the physico catalytic influence of such additive agents on the rate of crystal growth in the deposited metals is effected is somewhat beyond the province of this volume, and the reader is referred to standard books on colloids and electro-chemistry for the full discussion of this matter

ANODIC OXIDATION

In the discharge of anions such as OH' and the halogens at metal surfaces, the phenomenon of over-voltage has also been observed As a general rule the over-potential values obtained at the anode are smaller than the corresponding cathodic values, or the catalytic activity of the anode material is consequently higher

The following values were obtained by Coehn and Osaka in acid solution,[1] and by Foerster in an alkaline electrolyte [2]

Anode Material	Oxygen Over-voltage * (1)	Oxygen Over voltage * (2)	Halogen Over-voltage		
			Cl_2	Br_2	I_2
Nickel	0 05-0 12	0 38 0 56			
Cobalt	0 13				
Iron	0 24				
Platinised platinum	0 24	0 50-0 57			
Lead peroxide	0 28	0 44 0 86	0	0	0
Smooth platinum	0 44	1 46	0 47	0 33	0

* See Muller, *Zeitsch Elektrochem*, 1902, **8**, 426, Yamasaki *ibid*, 1910, **16**, 321

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[1] *Zeitsch anorg Chem*, 1903, **34**, 86

[2] *Zeitsch Elektrochem* 1904, **10**, 714

Foerster assumes the phenomena of anodic over-voltage to be due to the formation of an unstable oxide;[1] in the case of platinum a solid solution of the oxide PtO_3[2] in the metal is formed and a steady value for the over-potential is reached when equilibrium is established between oxide formation and decomposition.

The magnitude of the over-potential value is thus, according to Foerster, determined by the stability of the peroxide.

An application of the high anode over-potential value at a platinum surface is noted in the preparation of hypochlorites from a neutral aqueous solution of sodium chloride. The electrode potential of chlorine at one atmosphere in normal sodium chloride solution is about $-1{\cdot}37$ volts, whilst that of oxygen is only some $-0{\cdot}82$ volt. If it were not for the high over-potential value for oxygen rising to voltages greater than $-1{\cdot}46$ volts under a high current density and with a cold electrolyte, the preferential liberation of chlorine would not take place. The electrical efficiency of hypochlorite cells in which graphite electrodes are substituted for the more expensive platinum is usually somewhat low, part of the loss being due to the fact that the oxygen over-potential at a graphite anode is only sufficient to raise the electrode potential for oxygen discharge about 0·05 to 0·1 volt above that required for the liberation of chlorine. Dony Hénault[3] was able to effect the electrolytic oxidation of ethyl alcohol in sulphuric acid solutions either to acetaldehyde or to acetic acid by a rigorous control of the anode potential, $E_p = 1{\cdot}3$ volts in the former and 1·66 volts in the latter case.

The effect of agents added to the electrolyte.—As in the cases of electrolytic reduction, the addition of catalytic salts to the anolytes with the view of increasing the rate of oxidation as well as the electrical efficiency of the process has been the subject of various investigations. Amongst the more important polyvalent metallic salts which have been used for this purpose are those of vanadium, uranium, thallium, manganese, chromium, cerium, and occasionally copper, as well as certain anions, such as the halides, especially the fluoride ion.

In the electrolytic oxidation of sulphuric acid, suspensions of anthracene to anthraquinone, cerium sulphate, or chromic acid are usually employed as catalytic agents:

$$C_{14}H_{10} \rightarrow C_{14}H_8O_2,$$
$$Ce_2(SO_4) \rightarrow Ce(SO_4)_2.$$

Cerium sulphate[4] is much more active than chromic acid, and may be employed in a cell with no diaphragm between anode and cathode. With chromic acid, on the other hand, a divided cell must be employed to prevent cathodic reduction of the chromic acid. Since the electrolytic regeneration of the chromic acid does not usually keep pace with its reduction to chromium sulphate by means of the anthracene, the electrolyte containing the catalyst must be submitted to electrolytic oxidation from time to time

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[1] *Zeitsch. physikal. Chem*, 1904, **69**, 236, *Zeitsch. Elektrochem.*, 1910, **16**, 353.

[2] See Grube, *ibid*, 1910, **16**, 621.

[3] *Zeitsch Elektrochem.*, 1900, **6**, 533.

[4] See Le Blanc, *Zeitsch. Elektrochem*, 1900, **71**, 2903.

In the preparation of per-salts, such as persulphates, percarbonates, or perborates, the addition of a small quantity of a fluoride greatly enhances the yield[1] In this case, a high anode current density is usually employed with a metal exhibiting a high over-potential value for oxygen such as platinum, the function of the fluoride ion is undoubtedly to assist in elevating the value of the anode potential owing to the high value of its discharge potential In the Planté process of forming the positive electrodes of lead accumulator plates, the addition of small quantities of the chlorate ion considerably accelerates the rate of formation

Manganese salts[2] are likewise frequently employed to accelerate processes of electrolytic oxidation in organic compounds, such as the conversion of aniline to quinone

As in cases of electrolytic reduction, the nature of the anode material has a considerable influence on the yield, apart from the value of the oxygen over-potential or the effect of solution and re-precipitation of the metal

Brand and Ramsbottom[3] noted that the oxidation of manganates to permanganates proceeded more efficiently at nickel electrodes than at iron anodes, as suggested by Askenasy,[4] in spite of the lower oxygen over-potential of the former metal According to these investigators the mechanism of the oxidation is more complicated than a simple process of ionic transfer

$$MnO_4'' \rightleftarrows MnO_4' + \oplus,$$

and it appears that the presence of oxygen or a superoxide as a catalytic agent is essential for a high electrical efficiency Muller and Soller[5] observed the specific catalytic action of lead peroxide anodes in the oxidation of chromic salts to bichromates, $Cr^{\cdot\cdot\cdot} \longrightarrow CrO_4''$, a marked selective depolarising action of chromate solutions being obtained at the peroxide electrode, whilst at the surface of a platinum anode the electrode-electrolytic potential difference was actually raised by the addition of chromates Lead peroxide anodes, according to Muller,[6] likewise exert a catalytic action in the oxidation of iodates to periodates:

$$IO_3' \longrightarrow IO_4'$$

In various processes of electrolytic oxidation in organic chemistry lead peroxide anodes also exert a marked specific influence Thus, *p*-nitrotoluene can only be oxidised to *p*-nitrocresol at platinum anodes, but with lead peroxide as anode material, in spite of the lower oxygen over-potential, an almost quantitative yield of *p*-nitrobenzoic acid may be obtained.

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[1] See Muller and Friedberger, *Zeitsch Elektrochem*, 1902, **8**, 230

[2] D R P 117129/1900

[3] *J pr Chem*, 1910, **82**, 336

[4] *Zeitsch Elektrochem*, 1910, **16**, 170

[5] *Ibid*, 1905, **11**, 863

[6] *Zeitsch Elektrochem*, 1904, **10**, 61

PASSIVITY

According to Nernst we may attribute to all metals an electrolytic solution pressure, characteristic of the element. The difference of potential existing between a metal of electrolytic solution pressure, Ep, immersed in a solution of n valent ions of concentration C, is, as we have noted in the case of the hydrogen electrode, derived from a similar formula:

$$E = \frac{RT}{nF} \log \frac{Ep}{C}.$$

It follows that when a certain definite anode electrolyte difference of potential is exceeded, solution of the metal should occur, and likewise above a critical catholyte-cathode potential difference precipitation of the metallic ions should take place.

We have noticed that both hydrogen and oxygen show exceptions, the magnitude of the excess or over-potential above the theoretical being dependent on the nature of the electrode. It is extremely probable that similar cathodic over-potential phenomena are to be found in the electro-deposition of metallic ions, but the magnitudes of these discrepancies are usually extremely small. In the case of anodic solution of the metals, on the other hand, over-potentials may frequently assume quite large values, indicating a case of retardation in the anodic process:

$$M + \oplus \dashrightarrow \dot{M}.$$

The characteristic value of the electrolytic potential of a metal in a solution containing its ions is greatly influenced by the presence of other electrolytes in the solution

Cases of catalytic acceleration in the reaction $M + \oplus \dashrightarrow \dot{M}$ are extremely rare, although in the case of the anodic solution of tungsten metal the addition of hydroxyl ions appears to exert a catalytic activity in this direction

The investigations of the more common cases of negative catalysis in the reaction $M + \oplus \dashrightarrow \dot{M}$, resulting in an apparent reduction of the electrolytic solution pressure of the metal or an ennobling or passification of the element in the solution, are very extensive. The mechanism, however, by which passivity is brought about has not yet been thoroughly elucidated.

Keir[1] first observed that iron which had been treated with nitric acid lost its property of precipitating metals such as copper or silver from solutions of their salts. Schönbein[2] obtained similar results with iron which had been made the anode in an electrolytic cell. He likewise introduced the term "passivity". In the same year Faraday[1] advanced the so-called oxide film theory of passivity Faraday suggested that the passivity of a metal was essentially due to a surface oxidation process in which an invisible film of oxide was formed on the surface by immersion in oxidising solutions or by electrolytic processes

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[1] *Phil. Trans.*, 1790, **80**, 359.

[2] *Pogg. Ann.*, 1836, **37**, 340, 1837, **53**, 41, 1838, **43**, 103.

Later investigations have shown that many other metals exhibit this phenomenon, notably nickel, cobalt, chromium, platinum, tungsten, and molybdenum, whilst nearly all the other metallic elements possess the property to a minor degree

The work of Haber and Goldschmidt[2] on anodic polarisation in alkaline solution, of Muller and Spitzer[3] on the anodic polarisation of oxide films of iron cobalt and nickel, of Krassa[4] on passivity in strong alkalis, and of Grube[5] on the electrolytic oxidation of ferrocyanides at metallic anodes all lend considerable support to Faraday's theory

On the other hand Muller and Konigsberger[6] could not detect any difference in the reflecting powers of an active cathode and a passive anode, whilst if an anode film of even molecular dimensions had been present they stated that they would have been able to observe it Fredenhagen pointed out[7] that the oxide film theory appeared incompatible with the fact that the anodic potential of active and passive metals could assume apparently stable intermediate values, whilst Finkelstein[8] could find no evidence of an oxide film by measurements of condenser capacity Although all these criticisms have been ably met by the defenders of the oxide film theory, yet the alternative theories of Finkelstein and Le Blanc have both received considerable support

According to Finkelstein[9] and Kruger[10] the active and passive forms of the element are due to the presence of modifications of different valencies in the electrode Experimental proof of the existence of these modifications is wanting, although Hittorf[11] noted that active chromium dissolved in the divalent form, whilst passive chromium only went into solution in the hexavalent condition

Various investigators, on the other hand, have rejected the mechanistic theory of Faraday and the allotropic view advanced by Finkelstein, and have sought an explanation in the effect of catalytic acceleration and retardation of the primary anodic reaction

$$M+\oplus \longrightarrow M \longrightarrow \dot{M}\ nH_2O,$$

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[1] *Phil Mag*, 1836, 9, 53

[2] *Zeitsch Elektrochem*, 1906, **12**, 49

[3] *Zeitsch anorg Chem*, 1906, **50**, 321 See also Cohen, *Proc K Akad Wetensch Amst*, 1914, **17**, 680

[4] *Zeitsch Elektrochem*, 1909, **15**, 490

[5] *Idem*

[6] *Ibid*, 1907, **13** 659

[7] *Ibid*, 1909, **15**, 440

[8] *Ibid*, 1909, **15**, 490

[9] *Ibid*, 1907, **13**, 659

[10] *Ibid*, 1904, **10**, 832

[11] *Zeitsch physikal Chem*, 1900, **34**, 395.

a view originally propounded by Le Blanc,[1] who sought a solution in the relative speeds with which the ions were removed from the metal surface by hydration :

$$\dot{M} + nH_2O \longrightarrow \dot{M} \,.\, nH_2O.$$

Activation of a metal would thus entail an acceleration of the process of hydration.

Sackur [2] rejected Le Blanc's hypothesis of direct catalytic retardation of the primary anodic reaction and suggested that every metal, being in equilibrium with the hydrion in the solution, must of necessity contain some dissolved hydrogen :

$$2M + 2\dot{H} \rightleftarrows 2\dot{M} + H_2,$$

and passivity phenomena were caused by the slowness of the reaction between the dissolved hydrogen and the liberated anion. Fredenhagen, Muthmann, and Frauenberger [3] attribute passivity phenomena to the slowness of the reaction between the metal and the discharged anions :

$$4M + O_2 \longrightarrow 2M_2O \leftrightarrows 4\dot{M} + 2O'',$$

which results in the accumulation of gaseous oxygen in the electrode.

According to Foerster [4] all normal metals exist in the passive condition and only become active in the presence of a catalyst, whence we obtain a direct stimulation of the primary process of anodic solution :

$$M + \oplus \longrightarrow \dot{M}.$$

Evidence is given for assuming that molecular hydrogen is an active catalyst, whilst Grave [5] contends that the hydrogen ion is the primary catalyst in this reaction, since molecular hydrogen does not restore the activity to passive metals.

As a general rule, although intermediary values of the electrode potential between the active and the passive forms can be obtained and appear to be stable, yet actual transition from active to passive form or vice versa can frequently be accomplished with great rapidity, *e.g.* by touching passified metals with active metal. Schönbein, Ostwald, and Fechner noticed oscillations in both the gas discharge and the electromotive force of a cell formed of an active and a passive strip of the same metal. The periodic character and the influence of certain added electrolytes are strongly reminiscent of Bredig's experiments on the periodic decomposition of hydrogen peroxide at a mercury surface and of the electrical pulsations obtained by Lewis with mercuric cyanide in a capillary electrometer[1] Ostwald, as has already been noted (p 389), obtained a similar periodic evolution of hydrogen in the anodic solution of chromium[2] It must be admitted that both the Sackur and the Fredenhagen-Muthmann hypotheses appear very like the Faraday theory in the guise of ionic nomenclature Consequently there remain only three theories of passivity which may be regarded as fundamentally different in idea

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[1] *Zeitsch. physikal. Chem*, 1904, **48**, 577

[2] *Zeitsch. Elektrochem.*, 1908, **14**, 612 ; see also Haber and Zawadzki, *Zeitsch. physikal. Chem.*, 1911, **18**, 228.

[3] *Zeitsch. physikal. Chem.*, 1903, **43**, 1 ; 1908, **63**, 1 ; *Sitzungsber. K. Akad München*, 1904, **36**, 201.

[4] *Abh. d. Bunsen. Gesellschaft*, 1909, 2 ; *Zeitsch. Elektrochem.*, 1916, **22**, 85.

[5] *Zeitsch. physikal. Chem.*, 1911, **71**, 573.

(*a*) The passivity is due to the presence of oxygen in the electrode, as originally suggested by Faraday The oxygen may be present in solution as an alloy or as a compound, phenomena such as supersaturation accompanied by the sudden evolution of oxygen in the form of a gas film or liberation of an oxide as a separate phase may take place under conditions which induce a high degree of passivity The oxide or oxygen alloy film appears to be porous to the electrolyte or electrically conducting when formed under conditions inducing a low passivity This view has received considerable support by recent investigations on the passivity of metals in alcoholic electrolytes[3]

(*b*) Passivity is caused by the absence of a catalyst or the presence of a negative catalyst in the electrolyte inducing the rapid hydration of the discharged metallic anions

$$M + n(H_2O) \longrightarrow M, nH_2O$$

A rapid accumulation of non-hydrated ions would thus take place at the electrode surface, resulting in an increased polarisation

This view, originally suggested by Le Blanc, offers a ready interpretation of the effect of colloidal additive agents and of various alkaloids enhancing the passivity in solution The presence of oxidising agents is thus not necessary to produce the phenomenon of passivity

It may be noted that active polyvalent metals always dissolve in the form of the ions of lowest valency, and it may be reasonable to assume that such ions hydrate with a greater speed than those of higher valency, further, since a high degree of passivity produced by the chemical polarisation of the unhydrated ions is associated with the presence of an electrical double layer due to the charges on the ions between the electrode and film of electrolyte in juxtaposition to it, we may postulate that such a double layer may act as a condenser during discharge, thus accounting for the oscillatory nature of the rate of solution of passive elements, as noted by Ostwald Although capacity measurements to prove the existence of a condenser formed by such a double layer have yielded inconclusive results,[4] it might be cogently urged that the condenser plate in the liquid phase is extremely mobile and easily destroyed, thus precluding any such measurement

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[1] *Trans. Farad Soc*, 1912 **8**, 220

[2] *Zeitsch physikal Chem*, 1900 **35**, 33

[3] Izgaryschev, *J Russ Phys Chem Soc*, 1915, **47**, 1337

[4] See Schulze, *Zeitsch Elektrochem*, 1912, **18**, 326

(*c*) Passivity is the normal state of the elements, and activation is caused by the presence of a catalyst accelerating the velocity of the reaction:

$$M + \oplus \longrightarrow \dot{M}.$$

According to Foerster molecular hydrogen is such a catalyst, but more recent experiments have shown this view to be untenable. Grave's argument that the hydrogen ion is a specific catalyst for this reaction is open to serious criticism. It gives no explanation for the passifying action of nitric acid or the increased activation in the presence of halides, since the possible influence of the anions is not included in Grave's hypothesis.

Hittorf likewise noted that chromium readily became passive in hydriodic acid, and there is no simple relationship between increasing activity and increasing hydrion concentration.

CHAPTER XVI

CATALYSIS BY RADIANT ENERGY

THE increasing study of the influence of the various forms of radiant energy in the promotion of chemical reaction is resulting in the accumulation of a considerable number of processes in which the catalytic phenomena are completely manifest They may be characterised in general by the transformation of the radiant energy, most frequently from a higher to a lower vibrational frequency, with a simultaneous acceleration of reaction between the initial constituents, to yield the same end-products which result at a lower rate from the manifestation of the ordinary chemical forces of the system when uninfluenced by radiant energy

PHOTOCATALYTIC REACTIONS

Of such catalytic reactions, those induced by light may first be considered They comprise a most important subdivision of photochemical reactions, and from a study of several such photocatalytic reactions much of the knowledge of photochemical phenomena has been derived It is necessary to make quite clear at the outset the criteria of true photocatalytic reactions, since, otherwise, considerable confusion may result, light reactions being frequently complex and composite of several separate and distinct processes Photocatalytic reactions, in common with all catalytic processes, will yield the same end-products as the reaction unassisted by the catalyst The photocatalyst, therefore, accelerates the promotion of the ordinary equilibrium of a reaction This criterion rules out a number of reactions which on cursory examination might be regarded as photocatalytic Thus the ozonisation of oxygen at the ordinary temperature by ultra-violet light is not a catalytic process The reaction proceeds away from the chemical equilibrium at the given temperature The change is effected at the expense of light energy which is converted into chemical energy, an exact relation existing between the light energy absorbed and the chemical energy produced In the dark also the ozonised oxygen decomposes again to oxygen, and the original state is quantitatively reached after a finite interval of time. Similarly, the photochemical processes occurring in all plant life are frequently and wrongly assumed to be photocatalytic. Chlorophyll is not a catalyst of the processes of assimilation, since these are in essence the reduction of carbon dioxide:

$$x\mathrm{CO}_2 + x\mathrm{H}_2\mathrm{O} + \text{light} \longrightarrow \mathrm{C}_x\mathrm{H}_{2x}\mathrm{O}_x + x\mathrm{O}_2,$$

and at the ordinary temperature such a reaction is opposed in direction to that brought about by the operation of the ordinary chemical forces. Chlorophyll, therefore, must itself take part in the reaction. Not so, however, with certain other processes. Thus, for example, hydrogen and chlorine combine in the dark to yield hydrogen chloride. If the original system be suitably illuminated, reaction proceeds much more rapidly to the same end-product. It will be shown later that there is frequently an absence of proportionality between the light energy absorbed and the chemical energy produced; that is to say, a small amount of light is capable of bringing to reaction considerable amounts of the initial system.

Recently the term "photocatalysis" has been applied by Baly[1] to reactions which are, in reality, cases of photosensitisation. They include the processes of carbohydrate synthesis discussed above and other reactions which are opposed to the normal free energy factors; but they also include photosensitised spontaneous reactions, as, for example, the photodecomposition of nitrogen pentoxide. The pure compound is not sensitive to blue light, but becomes so when some nitrogen dioxide is present to absorb this blue light.[2] Such sensitisations of chemical reactions to light by admixture of light-adsorbing agents have been known for a long time. Their most important use is in the sensitisation of photographic plates, by bathing these in a suitable dye.[3] They are of importance also in biological processes, since, as was shown by Tappeiner and Jodlbauer,[4] bacteria can be rendered sensitive to illumination by treatment with fluorescent substances. Weigert showed also that in gaseous systems such photosensitisation could be produced.[5] Thus phosgene, which is a colourless gas absorbing in the ultra-violet only, can be made sensitive to visible light by admixture of chlorine. This latter gas also sensitises, to visible light, the decomposition of ozone, the combination of hydrogen and oxygen and of sulphur dioxide and oxygen. It is eminently desirable to group all such processes under the general term "photosensitisation" rather than to call them, with Baly, cases of photocatalysis.

The hydrogen-chlorine combination.—Historically regarded, the interaction of hydrogen and chlorine is at once the most important of photochemical reactions in general and of photocatalytic reactions in particular. The acceleration of combination of these gases due to light was observed as early as 1801 by Cruickshank.[1] The phenomenon received further investigation from Gay-Lussac and Thenard,[2] and from Dalton,[3] who showed that the reaction could proceed with explosive violence. A quantitative investigation was undertaken by Draper[4] and yielded a most important contribution to photochemical knowledge. Thus Draper enunciated, as a result of his investigations, his now well-known Law of Absorption, which may be expressed briefly in the statement that "Only those light rays which are absorbed by a chemical system are photochemically active." This law had previously been stated, from a theoretical standpoint, by Grotthus in 1818.

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[1] *Brit. Assoc. Reports*, "On Absorption Spectra"; Baly, Heilbron, and Barker, *J. Chem. Soc.*, 1921, **119**, 1025.

[2] Daniels and Johnston, *J. Amer. Chem. Soc.*, 1921, **43**, 72.

[3] Vogel, *Ber.*, 1873, **6**, 1305.

[4] *Die sensibilisierende Wirkung fluorescierender Substanzen*, Leipzig, 1907.

[5] *Ann. Physik*, 1907 (4), **24**, 55, 243.

Draper constructed an apparatus for measuring the intensity of the absorbed rays, terming it a Tithonometer, which consisted simply of a U-tube closed at one end and partially filled with a mixture of hydrogen and chlorine obtained by electrolysis of hydrochloric acid, the gases being stored over hydrochloric acid. On illumination the gases combined to form hydrogen chloride, which dissolved in the containing liquid, the alteration in level of the meniscus giving a measure of the light energy consumed. In the classical researches of Bunsen and Roscoe,[5] on the quantitative value of the hydrogen-chlorine reaction, the apparatus of Draper was improved. The gases were contained in a suitable vessel with parallel plane surfaces, and were stored over water saturated with the gas mixture. Measurement of the contraction occurring on solution of the hydrogen chloride formed by the reaction was made in a horizontal capillary with attached scale, the meniscus being formed by a thread of water. The displacement of the thread of liquid was governed by the intensity of the illumination and the diameter of the capillary tube, so that by making this latter narrow a large displacement of the meniscus could be effected by even weak illumination. A diagrammatic representation of a modified form of Bunsen-Roscoe actinometer is given in Fig. 24. It was used by Burgess and Chapman in the researches later to be detailed, and possesses, in addition, a float contrivance for registering small fluctuations over long periods by means of a lever arm operating a pointer on smoked paper.

The results of the Bunsen-Roscoe study may be summarised. It was shown that the ordinary laws of optics were applicable to the light rays absorbed. The reaction occurring was inversely proportional to the square of the distance from the source of illumination. The laws of reflection and the Beer-Lambert Law of Absorption were likewise applicable. The existence of an induction period, first noted by Cruickshank, and during which the gases increased in reactivity to a maximum, was exhaustively studied. Bunsen and Roscoe showed that the sensitivity of the gases to light was extremely small in the early stages of passage through the "actinometer". On continued passage, the sensitivity increased to a fairly reproducible maximum, attained after three to six days' passage of gas. They showed that it was necessary to remove air as completely as possible, as the presence of oxygen affected the sensitivity of the gas mixture enormously. Thus the presence of 0·5 per cent of oxygen lowered the sensitivity in the ratio of 10 to 1. The induction period was shown to depend upon the depth of gas-layer illuminated. Also it was shown to be shorter if the light intensity was increased The length of the induction period was governed also by the previous history of the reacting gas mixture, being greatest with fresh gas and short if the gases had been previously illuminated.

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[1] *Nicholson's Journal*, 1801 (i.), **5**, 202.
[2] 1810.
[3] *New System of Chemical Philosophy*, 1811.
[4] *Phil. Mag.*, 1841, **19**, 195; 1843, **23**, 401; 1845, **27**, 327.
[5] *Pogg. Ann.*, 1855, **96**; 1857, **100**, **101**; 1859, **108**.

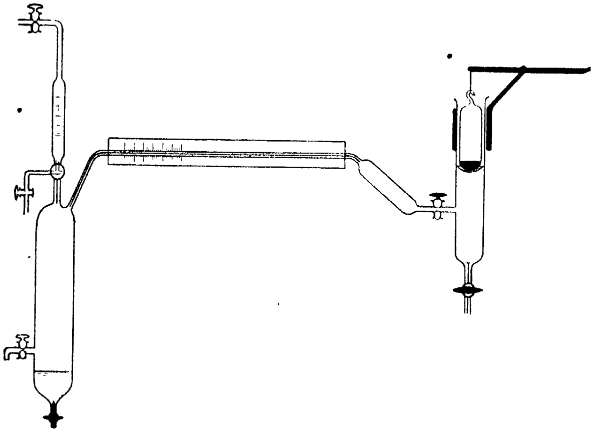

FIG. 24.

The phenomenon of induction has been frequently studied since the work of Bunsen and Roscoe, and has led to a complete explanation. Pringsheim[1] attributed the retarding action of oxygen to the formation of intermediately formed hypochlorous acid, but Mellor[2] showed this to be untenable, since neither Cl_2O nor hypochlorous acid affected the period of induction. The researches of Burgess and Chapman,[3] and of

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[1] *Wied. Ann.*, 1887, **32**, 384.

[2] *J. Chem. Soc.*, 1902, **81**, 1293.

[3] *Ibid.*, 1906, **89**, 1402.

Chapman and MacMahon,[1] established conclusively the real causes of the induction period. These workers showed that the existence of a period of retarded action was always conditioned by the presence of foreign substances already in the containing liquid or on the glass vessels or introduced through the taps. It was not a function of oxygen content of the gas—this only retarded the reaction velocity, but did not affect the length of the induction period. Even oxidising agents such as nitric acid, hydrogen peroxide, or potassium permanganate had no marked influence on the induction. The slightest traces of ammonia, however, prolonged the induction period enormously, and, with very small amounts, the period was proportional to the amount present. The compounds NCl_3, $NOCl$, ClO_2, and NO_2 similarly retarded reaction enormously, but, on the other hand, Cl_2O and N_2O were found to be innocuous, pointing to the operation of specific chemical reaction with the hydrogen-chlorine mixture. Similarly, organic nitrogen compounds such as albumin acted like ammonia. It is evident, therefore, that in the early period of illumination of a hydrogen-chlorine mixture part of the light energy is consumed in removal, by chlorination, of the impurities present in the reaction vessel and that the constant maximum reaction velocity represents a state of affairs in which the introduction and removal by chlorination of impurities has reached an equilibrium condition. Obviously, also, if precautions be taken against introduction of impurities and those originally in the containing vessel be removed by illumination of the reaction system, it follows that the induction period would no longer be observed. This was demonstrated by Burgess and Chapman in a simple quartz-glass actinometer, and also by Bodenstein in a series of researches later to be discussed. In the absence of impurities of the types mentioned, the induction period completely disappears.

Baly and Barker have recently claimed[2] that complete removal of impurities does not eliminate entirely the induction period. In their view, which will be amplified in the subsequent discussion, the hydrogen chloride produced in the process acts as a source of energy for the reaction of further molecules of hydrogen and chlorine. As the quantity of hydrogen chloride produced per unit of time increases, the reaction should become faster and faster by increase in the transfer of such energy to reactant molecules; a stationary state would be attained when an equilibrium is established between loss of energy by radiation and transference to reactants on the one hand, and energy yield by illumination and reaction on the other. It should be emphasised, however, by way of caution, that the presence of minute quantities of impurities in the Baly-Barker reaction system would lead to experimental results of the type obtained by them, so that evidence for the correctness of their viewpoint as to energy transfer from resultants to reactants should be obtained from other sources. Weigert has suggested[1] that impurities may have influenced the Baly-Barker experimental results.

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[1] *Loc. cit.*, 1909, 97, 845.

[2] *J. Chem. Soc.*, 1921, 119, 653.

Weigert and Kellermann[2] have decisively demonstrated by experimental methods the existence of an induction period in the hydrogen-chlorine reaction—of much shorter duration, however, than those previously discovered. The hydrogen chloride produced on illumination from a momentary intense spark is not produced instantaneously, but in an after-effect occurring approximately $\frac{1}{100}$ second after illumination. The purer the gas mixture the larger the duration of the after-effect. For such an effect to be observed it is evidently necessary that a hydrogen-chlorine mixture be illuminated, since Bodenstein and Taylor[3] showed that chlorine, mixed with hydrogen $\frac{1}{1000}$ second after illumination of the chlorine, had quite lost its reactivity. This was also found by Vollmer[4] for a somewhat longer time interval between illumination of the chlorine and admixture with the hydrogen.

Kinetics.—In the investigations of Chapman and his co-workers,[5] as in most of the later work on the hydrogen-chlorine reaction, the technique of Bunsen and Roscoe has been followed. The limitations of the actinometer for purposes of investigation are marked. Bodenstein and Dux,[6] however, by the employment of an ingenious method of measurement of reaction velocity, contributed materially to the solution of this problem. These workers adapted a method of measurement which eliminated the necessity of employing water as absorbent for the hydrochloric acid formed. Instead, the progress of the reaction under illumination was followed by freezing out with liquid air the residual chlorine and the hydrogen chloride formed during exposure to light, the partial pressure of the unused hydrogen being then measured at temperatures determined by means of an oxygen thermometer. In this manner the photochemical combination of hydrogen and chlorine in varying molecular proportions, and with variable concentrations of oxygen, hydrogen chloride, and water vapour, was exhaustively studied. It was thus established that:

(1) The combination of hydrogen and chlorine under the influence of light is a reaction of the second order, the velocity being proportional to the square of the chlorine concentration. Hydrogen is without influence so long as it is present to the extent of at least one-quarter of the volume of chlorine. At smaller hydrogen concentrations the velocity decreases slightly.

(2) The hydrochloric acid formed is without influence on the velocity.

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[1] *Zeitsch. physikal. Chem.*, 1923, **106**, 428. See also Marshall, *J. Physical Chem.*, 1925, **29**, 1453.

[2] *Sitzungsber. preuss. Akad.*, 1922, 315; *Zeitsch. Elektrochem.*, 1922, **28**, 456; *Zeitsch. physikal. Chem.*, 1923, **107**, 1.

[3] *Zeitsch. Elektrochem.*, 1916, **22**, 202.

[4] *Zeitsch. Elektrochem.*, 1914, **20**, 494.

[5] Chapman and Burgess, *loc. cit.*; Chapman and MacMahon, *J. Chem. Soc.*, 1909, **95**, 135, 959; Chapman and Underhill, *ibid.*, 1913, **103**, 496.

[6] *Zeitsch. physikal. Chem.*, 1913, **85**, 297.

(3) Water vapour within certain limits (0·004-2·3 mm.) is also without influence.

(4) Oxygen retards the reaction in such a way that the velocity, at all stages of the combination, is inversely proportional to the concentration of oxygen.

It is obvious that the equation of the reaction of the system may therefore be represented by the expression

$$+\frac{d[2HCl]}{dt}=k\frac{I_0[Cl_2]^2}{O_2},$$

where the quantities in brackets denote concentrations of gases, I_0 the light absorbed, put proportional to reaction rate in agreement with Bunsen and Roscoe, t the reaction time.

Chapman and Whiston[1] dispute the conclusions of Bodenstein and Dux and ascribe their results to the operation of inhibitors in the reaction system. A recent study of the kinetics by M. C. C. Chapman[2] leads to the following conclusions:

(1) The rate of combination of the hydrogen and chlorine, in mixtures of electrolytic hydrogen and chlorine and oxygen, is nearly independent of the pressure of the gas.

(2) In mixtures in which the concentrations of the hydrogen and the oxygen are kept constant, the rate of combination is

(*a*) Proportional to the first power of the concentration of the chlorine when the proportion of hydrogen is small;

(*b*) Proportional to a power of the concentration of the chlorine between the first and the second when a moderate proportion of hydrogen is present;

(*c*) Proportional to the square of the concentration of the chlorine when the proportion of chlorine is small and that of the hydrogen large.

(3) In mixtures in which the concentrations of the chlorine and oxygen are kept constant, the rate of combination is

(*a*) Proportional to the concentration of the hydrogen when the proportion of hydrogen is small;

(*b*) Inversely proportional to a power of the concentration of the hydrogen, which is rather less than 1·2 when the proportions of hydrogen and chlorine are moderate;

(*c*) Inversely proportional to a power of the concentration of the hydrogen, which is rather less than 1 when the proportion of chlorine is small.

(4) The rate of combination is independent of the concentration of the oxygen in mixtures in which the concentration of the hydrogen is very small; for all other mixtures it is inversely proportional to the

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[1] *J. Chem. Soc.*, 1919, **115**, 1264.

[2] *J. Chem. Soc.*, 1923, **123**, 3062.

concentration of the oxygen. The results can be summarised by the formula

$$\frac{d[\mathrm{HCl}]}{dt}=\frac{k_1[\mathrm{H_2}][\mathrm{Cl_2}]^2}{k_3[\mathrm{H_2}]^{2\cdot x}[\mathrm{O_2}]+[\mathrm{Cl_2}]}.$$

It is also concluded that the observed inhibitive effects of oxygen and of hydrogen are not—as has been hitherto assumed—due to the direct and independent action of these gases, but to the joint agency of both.

The absence of influence of water vapour within the limits above mentioned does not extend to extremely dry gases. Baker[1] and, later, Mellor and Russell[2] showed that hydrogen and chlorine, when thoroughly dried over phosphorus pentoxide, only slowly reacted in bright sunlight. There was a possibility that, in these experiments, long drying over phosphorus pentoxide might have introduced some inhibitors, *e.g.*, oxygen into the reaction system, which would account for the retardation observed. This possibility has been eliminated by recent work of Tramm,[3] who, using modern low temperature technique for the drying of gases by liquefaction and fractional distillation, showed that a hydrogen-chlorine mixture so dried was inactive photochemically. The introduction of a small amount of water vapour made a mixture so dried normally photosensitive. The inertness of dried hydrogen-chlorine mixture is confined, however, to the visible and near ultra-violet region of the spectrum. Coehn and Jung have recently shown[4] that a dry mixture, quite inert to daylight for twenty days or to illumination for forty minutes at 15 cm. distance from a 100-candle-power osram lamp, is quantitatively converted to hydrogen chloride when exposed for twelve minutes at 20 cm distance from a quartz mercury vapour lamp. A screen of uviol glass, whose transmission extends to 2540 Å., was sufficient to protect the reaction mixture in a quartz tube from reaction. It is evident, therefore, that the wave-length active in causing the combination of a dried hydrogen-chlorine mixture lies between 2200 and 2540 Å

Energetics.—The reaction is one which shows large deviation from the Einstein law of photochemical equivalence. Bodenstein calculated that in his most sensitive gas mixtures as many as 10^6 molecules of chlorine react for every quantum of light energy absorbed The work of Baly and Barker, already cited, indicates that the deviations from Einstein's law become more pronounced the greater the intensity of illumination, since they found that the maximum reaction velocity increased more rapidly than the intensity of illumination. Marshall[5] has recently shown that the quantum yield decreases enormously at pressures below 6 cm.

The disproportionality between chemical energy and light energy absorbed is confirmed by investigations of Taylor[1] on the interaction of hydrogen and chlorine under the influence of α-particles, and by investigations of Le Blanc and Vollmer[2] on the same reaction under the influence of Rontgen rays In each of these cases chlorine to the extent of 10^4 molecules or more is brought into combination by every pair of ions produced in the reaction system by either type of radiation

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[1] *J. Chem. Soc.*, 1894, **65**, 611.

[2] *Ibid*, 1902, **81**, 1279.

[3] *Zeitsch physikal. Chem.*, 1923, **105**, 356

[4] *Ber*, 1923, **56**, 696.

[5] *J. Physical Chem.*, 1925, **29**, 1453.

Theories of mechanism—Any satisfactory theory of the mechanism of the hydrogen-chlorine combination must supply an explanation for a variety of phenomena Of these the principal are the induction period of Weigert and Kellermann, the inhibitory influence of oxygen, the necessity for water vapour in illumination by visible light, the sensitivity to ultra-violet light in the absence of water vapour, the abnormal ratio of reactant molecules to absorbed energy The order of the reaction as to chlorine is important, but, as already emphasised, the experimental evidence on this point is not unequivocal The attempts at a satisfactory theory of mechanism are legion Only the more recent can be considered

As the outcome of the Bodenstein-Dux investigation, Bodenstein suggested a reaction mechanism involving a photoelectric effect on the chlorine as a primary process The electron thereby expelled became the catalyst in a series of processes which may be indicated in the equations

$$\begin{aligned} &(1)\ Cl_2 + \text{light energy} = Cl_2^{+} + \ominus, \\ &(2)\ Cl_2 + \ominus = Cl_2\ , \\ &(3)\ Cl_2^{-} + H_2 = 2HCl + \ominus \end{aligned}$$

A succession of reactions (2) and (3) involving alternate capture and release by reaction of an electron would have accounted for the high yield per unit of absorbed energy Bodenstein also showed that it was in accord with his kinetic equation Failure to detect ionisation in illuminated chlorine[3] led Bodenstein, in spite of the evidence already cited concerning the action of α-particles and Rontgen rays, to adopt a reaction mechanism based upon the transfer of energy from energy-rich hydrogen chloride molecules to either chlorine or oxygen molecules, but not to hydrogen or nitrogen molecules Bodenstein saw in the ultra-violet absorption spectra of these gases justification for this view His new formulation[4] of the reaction mechanism is embodied in the following set of equations

$$Cl_2 + \text{light} + H_2 = 2HCl(b)$$

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[1] *J Amer Chem Soc*, 1915, **37**, 24, 1916, 38, 280

[2] *Zeitsch Elektrochem*, 1914 **20**, 494

[3] Thomson, *Proc Camb Phil Soc*, 1901, **11**, 901, Le Blanc and Vollmer, *Zeitsch Elektrochem*, **1914, 20**, 494, Kummell, *Zeitsch Elektrochem*, 1911, **17**, 490

[4] *Zeitsch Elektrochem*, 1916, **22**, 58

The (b) indicates that the molecule is possessed of an abnormally high energy content. The loss of this energy is assumed to occur as follows:

$$\begin{array}{ll}
\mathrm{HCl}(b) = \mathrm{HCl}. \quad . \quad . & (\text{Constant} = k_3), \\
\mathrm{HCl}(b) + \mathrm{O}_2 = \mathrm{HCl} + \mathrm{O}_2(b) & (\text{Constant} = k_4), \\
\mathrm{O}_2(b) = \mathrm{O}_2, & \\
\mathrm{HCl}(b) + \mathrm{Cl}_2 = \mathrm{HCl} + \mathrm{Cl}_2(b) & (\text{Constant} = k_5), \\
\mathrm{Cl}_2(b) = \mathrm{Cl}_2 \quad . \quad . \quad . & (\text{Constant} = k_7), \\
\mathrm{Cl}_2(b) + \mathrm{H}_2 = 2\mathrm{HCl}(b) \quad . & (\text{Constant} = k_8).
\end{array}$$

The $2\mathrm{HCl}(b)$ can then repeat one or other of the preceding changes. The kinetic interpretation of these equations leads to the following set of reaction velocity equations:

$$+\frac{d[2\mathrm{HCl}(b)]}{dt} + = k_2 \mathrm{I}_0[\mathrm{Cl}_2] + k_8[\mathrm{Cl}_2(b)][\mathrm{H}_2],$$

$$-\frac{d[\mathrm{HCl}(b)]}{dt} = k_3[2\mathrm{HCl}(b)] + k_4[\mathrm{HCl}(b)][\mathrm{O}_2] + k_5[\mathrm{HCl}(b)][\mathrm{Cl}_2],$$

$$+\frac{d[\mathrm{Cl}_2(b)]}{dt} = k_5[\mathrm{HCl}(b)][\mathrm{Cl}_2],$$

$$-\frac{d[\mathrm{Cl}_2(b)]}{dt} = k_7[\mathrm{Cl}_2(b)] + k_8[\mathrm{Cl}_2(b)][\mathrm{H}_2].$$

From these equations the measured reaction velocity equation may be deduced if k_8 be extremely large—which is suggested by the small influence of hydrogen—and yields

$$-\frac{d[\mathrm{H}_2]}{dt} = k_2 \frac{k_5 \mathrm{I}_0[\mathrm{Cl}_2]^2}{k_3 + k_4[\mathrm{O}_2]},$$

which is in agreement with the experimental results of Bodenstein and Dux provided k_3 is small compared with $k_4\mathrm{O}_2$. The presence of k_3, the constant for energy loss from activated chlorine, prevents the equation for the velocity from becoming infinite at zero oxygen concentration. We shall see in later sections that there is a definite trend of opinion recently towards some type of energy transfer of the type herein assumed. This represents an early effort to link up such a mechanism with the kinetic studies.

Chapman and Whiston assume that the radiation absorbed by chlorine can be lost by impact with oxygen molecules; but, when the pressure of hydrogen exceeds 15 cm., and possibly at lower pressures, almost all the active molecules of chlorine—the concentration of which is dependent on the oxygen concentration—combine with hydrogen. They derive an equation

$$+\frac{d2\mathrm{HCl}}{dt} = k \frac{\mathrm{I}_0[\mathrm{Cl}_2]}{[\mathrm{O}_2] + k_5[\mathrm{H}_2]},$$

which is in agreement with their experimental measurements, since k_5 is of small magnitude, being an expression of Chapman and Underhill's observation that hydrogen is a weak inhibitor This equation offers no solution, however, for the abnormal photochemical yield of the process

D L and M C C Chapman[1] conclude that active chlorine is not deactivated by oxygen alone, but by the joint agency of hydrogen and oxygen They suppose that the active energy is shared between the oxygen and the chlorine, and the hydrogen can rapidly remove it from the oxygen They state that the simplest hypothesis is that the active oxygen combines with hydrogen to produce water, the active energy being simultaneously degraded Their hypothesis of the combination of hydrogen and active chlorine implies that the degradation of energy which occurs when hydrogen combines with active chlorine is negligible.

The abnormal yield of the hydrogen-chlorine reaction led Nernst to propose[2] a mechanism in which the primary photochemical process was assumed to be a splitting of a chlorine molecule into atoms This primary process was then assumed to be succeeded by a chain of reactions resulting in the abnormal yield In agreement with the observations of Stern and Vollmer, already discussed, we may write the primary process as occurring through the energy-rich chlorine molecule Cl_2b, thus

$$Cl_2 + h\nu = Cl_2b = 2Cl$$

The chain reactions which succeed this elementary process are, according to Nernst

$$Cl + H_2 = HCl + H,$$
$$H + Cl_2 = HCl + Cl$$

Nernst showed, by thermodynamic reasoning, that both of these reactions are accompanied by free energy decrease, and therefore can occur spontaneously They therefore give rise to a chain of reactions resulting in hydrogen chloride formation, which sequence is only stopped by removal of the active atoms by collision with each other or by reaction with oxygen or other inhibitor

This reasoning suggested that, were a suitable acceptor for chlorine atoms present, no chain reactions would ensue and the law of the photochemical equivalent would be fulfilled This was realised in Nernst's laboratory, the action of chlorine on trichlorbrommethane being shown by Noddack[3] to be photosensitive and obeying the equivalent law The action of bromine on hexahydrobenzene was, in the course of the same investigations, shown by Pusch[4] to be in agreement with the Einstein law

Coehn's interpretation of the chain reactions is a modification of

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[1] *J Chem Soc*, 1923, **123**, 3079

[2] *Zeitsch Elektrochem*, 1918, **24**, 335.

[3] *Zeitsch Elektrochem*, 1921, **27**, 359

[4] *Zeitsch Elektrochem*, 1918, **24**, 337

Nernst's, to take account of the different sensitivities of the dried gases to visible and ultra-violet light. Weigert[1] objects to Coehn's chain mechanism for the moist gases, since it involves water molecules in the chain mechanism and therefore in the yield of the process and the reaction velocity. The data of Bodenstein and Dux as to the absence of effect of water vapour between wide limits contradicts this. Weigert therefore assumes water to be a component of the primary photochemical system, which must be a mixture of the gases in agreement with the observations of Bodenstein and Taylor and of Vollmer. Weigert therefore assumes, in agreement with an earlier proposal of Mellor,[2] that, for the primary process, chlorine, hydrogen, and water vapour must be present, forming a light sensitive system. The primary process is then, according to Weigert, an inner photoelectric effect between a hydrogen and a chlorine molecule leading to the formation of gas ions, thus:

$$\mathrm{H}_2 + h\nu + \mathrm{Cl}_2 = \mathrm{H}_2^{+} + \mathrm{Cl}_2 ,$$

which is then followed by

$$\mathrm{H}_2^{+} + \mathrm{Cl}_2^{-} = \mathrm{HCl} + \mathrm{H} + \mathrm{Cl},$$

$$\left.\begin{array}{ll} & \mathrm{H} + \mathrm{Cl} = \mathrm{HCl} \\ 2\mathrm{H} = \mathrm{H}_2 ; & 2\mathrm{Cl} = \mathrm{Cl}_2 \end{array}\right\} \text{or the Nernst chain mechanism}$$

Weigert assumes that the water vapour intensifies this effect by forming adsorption complexes with the other two gases, bringing the hydrogen and chlorine molecules into closer proximity. With respect to the inner photoelectric effect, it is apparent that the light must activate the hydrogen in some way. Weigert points out that, although hydrogen of itself absorbs only in the extreme ultra-violet, a molecule in the immediate neighbourhood of a chlorine molecule with a large electron affinity may be made to yield an electron by a lesser quantum, whose magnitude is smaller the nearer the two molecules are.[3]

Baly and Barker's explanation[4] of the abnormal yield is practically identical with that of Bodenstein already cited. They assume, however, transference of energy from energy-rich hydrogen chloride molecules to hydrogen as well as to chlorine. This is not in accord with the kinetic studies, which show that the reaction rate is independent of the hydrogen concentration over considerable ranges.

Experimental confirmation of the Nernst chain mechanism was sought by Bodenstein[5] in some recent work relative to the permeability of iron to hydrogen. The hydrogen diffuses through the metal in the atomic condition. Bodenstein attempted to initiate the hydrogen-chlorine reaction by trying to release hydrogen atoms from the iron into the gaseous system. The experiments gave negative results;

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[1] *Zeitsch. physikal Chem.*, 1923, **106**, 426.

[2] *J. Chem. Soc.*, 1902, **81**, 1293.

[3] Cf. also Ludlam, *Phil. Mag.*, 1912, **23**, 757.

[4] *J. Chem. Soc.*, 1921, **119**, 653.

[5] *Zeitsch. Elektrochem.*, 1922, **28**, 517.

this should have been expected, since it is generally accepted, as a result of the experimental work of Langmuir, that hydrogen never leaves a metal surface in the atomic condition Definite proof that one step in the Nernst chain mechanism actually can occur has been recently obtained by Marshall and Taylor[1] They have shown that hydrogen atoms, produced by R W Wood's method,[2] the passage of a high-tension powerful discharge (25,000 volts, 0 12 amp) through hydrogen at low partial pressures, when led into unilluminated chlorine, give measurable quantities of hydrogen chloride More recent measurements with varying hydrogen pressure have led Marshall to the conclusion[3] that the experimental results with hydrogen atoms are more in accord with the concept of energy-rich chlorine molecules

Further photocatalytic halogenations. The accelerating action of light is demonstrable in many other processes of halogenation Thus the combination of carbon monoxide, of sulphur dioxide, of saturated, unsaturated, and aromatic hydrocarbons, of organic acids, such as acetic acid, with chlorine and the other halogens, may all be stimulated by illumination, and the study of such actions has increased the material at the disposal of the theoretical investigator and has contributed to possible technical development

The photocatalytic combination of carbon monoxide and chlorine was first observed by Davy[4] and studied quantitatively by Dyson and Harden,[5] by Wildermann,[6] by Weigert,[7] and by Chapman and Gee[8] The reaction is much less sensitive to light than the hydrogen-chlorine combination, strong illumination causing but weak reaction Oxygen also inhibits the reaction, and, as was shown by Chapman and Gee, in a remarkable way The first additions of oxygen have a strongly inhibitive effect, which decreases with further additions, so that with half an atmosphere of oxygen the reaction is but little slower than in presence of one-quarter of an atmosphere The sensitivity, S, could be expressed by an equation

$$S = A + \frac{B}{[O_2]},$$

where A and B are constants, $[O_2]$ the oxygen concentration Wildermann concludes from a small series of measurements that the reaction is the usual one of the second order

$$\frac{dx}{dt} = k[Cl_2][CO]$$

Bodenstein has discussed these results from the point of view of his electronic theory, and shows that the deviations from the hydrogen chlorine reaction are to be sought in the relative non-reactivity of the carbon monoxide with the activated chlorine. He calculates that in the carefully prepared mixture of gases employed by Wildermann 100 molecules of chlorine react per light quantum. Moreover, he observes that by increase of oxygen concentration it should be possible almost completely to suppress the secondary reaction which leads to the disproportionality between light energy and chemical energy observed in the hydrogen chlorine reaction, and thereby to emphasise the primary reaction in which proportionality exists. An investigation of such points of interest is promised.

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[1] *Nature*, 1923, **112**, 937

[2] *Proc Roy Soc*, 1922 **102A**, 1

[3] *J Physical Chem*, 1925, **29**, 842 See also Marshall, *Trans Am Electrochem Soc*, April 1926

[4] *Phil Trans*, 1812 **144**

[5] *J Chem Soc*, 1903, **83**, 201

[6] *Phil Trans* 1902, **199A**, 337

[7] *Ann Physik*, 1907, **24**, 55

[8] *J Chem Soc*, 1911, **99**, 1726

In the production of phosgene from carbon monoxide and chlorine in the presence of oxygen it has been shown that carbon dioxide is formed. Phosgene therefore sensitises this reaction to visible light. Weigert suggested that this was to be attributed to the action of radiation produced in the phosgene synthesis. Kornfeld and Birnbaum[1] have shown, however, that this is not so, since the reaction to form phosgene proceeding in a gas space surrounding a quartz vessel containing carbon monoxide and oxygen failed to produce any combination of these latter gases. The sensitisation of the carbon dioxide reaction must therefore be due to kinetic energy transfers and not to radiation phenomena, a conclusion of importance in view of the data of photosensitisation later to be discussed.

It is of interest to record that, as a result of a research recently published by Bodenstein and Plaut,[2] the thermal production of phosgene is independent of the oxygen concentration but is catalysed by the chlorine, the velocity data being completely reconcilable with a reaction scheme:

$$(1) \quad Cl_2 = 2Cl,$$

$$(2) \quad Cl + Cl_2 = Cl_3,$$

$$(3) \quad Cl_3 + CO = COCl_2 + Cl.$$

The processes (1) and (2) represent equilibria continuously maintained. The velocity is to be attributed to process (3). Bodenstein hopes subsequently to reconcile the observations made on both thermal and photochemical reactions.

The photocatalytic halogenation of the hydrocarbons has been most exhaustively studied in reference to the aromatic hydrocarbons. Luther and Goldberg[3] observed, in the chlorination of benzene, toluene, and xylene, strong inhibition of the catalytic process due to oxygen. Bruner and Czernecki[4] have shown that bromination is also sensitive to oxygen, and leads to quite indefinite rates of reaction unless the oxygen is removed. Addition of iodine to the system in determined amounts effects the removal of oxygen, by reaction to yield oxy-iodine compounds. In absence of oxygen, bromination occurs in the side chain at a velocity proportional to the intensity of the light I_0 and the concentration of hydrocarbon present, thus.

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[1] *Zeitsch. physikal. Chem.*, 1924, **108**, 118.

[2] *Zeitsch. physikal. Chem.*, 1924, **110**, 399.

[3] *Zeitsch. physikal. Chem.*, 1906, **56**, 43.

[4] *Bull. Acad. Sci. Cracow*, (*A*), 1910, 576.

$$\frac{dx}{dt}=kI_0(C_7H_8)$$

That the bromine concentration was without influence was shown by the authors to be due to the experimental arrangements, in which absorption of the light was practically complete even in moderate concentrations. For a homogeneous field of illumination—in other words, with weak absorption—the reaction velocity equation would be

$$\frac{dx}{dt}=kI_0(Br_2)(C_7H_8)$$

The yield of reaction per quantum of energy absorbed is high when oxygen has been displaced from the system. According to Bodenstein this can be estimated at 10^6 molecules reacting per quantum of energy absorbed.

The temperature coefficient of the photochemical reaction between bromine and toluene is also of interest. Normally, photochemical reactions possess a very small temperature coefficient. Thus Bunsen and Roscoe determined the coefficient for hydrogen-chlorine combination as 1·2 per 10°, whilst later measurements of Roscoe and Denison gave unity. In other words, elevation of temperature normally promotes but little the velocity of a photochemical reaction. In the photo-bromination of toluene, however, the temperature coefficient possesses the relatively high value of 1·85. The corresponding reaction in the dark likewise possesses the high temperature coefficient of 4, as opposed to the normal value of 2-3. Bodenstein interprets this on the assumption that both bromine and toluene must be active in order to react upon collision (or, interpreted in the recent phraseology of energetics, both molecules must receive a definite critical increment of energy before reaction occurs).[1] In the light reaction the temperature coefficient 1·85 represents the increase, for temperature rise of 10°, of active molecules of toluene, whilst 4·0/1·8 = 2·2 represents the increase in active bromine molecules. In this manner, it is suggested, an increase in our knowledge of ordinary chemical processes may result from a study of photochemical reactions.

It is of interest to record that the combination of hydrogen and bromine is only very slightly sensitive to light at ordinary temperatures, but becomes markedly so at temperatures of 150° C. and upwards.[2] Bodenstein and Lutkemeyer have examined this reaction in detail and show that the increased velocity is to be attributed to the formation of bromine atoms by absorption of light. This research has already been discussed in an earlier chapter (p. 148) with reference to the inhibitory action of hydrogen bromide and iodine, effects which are common both to the light and dark reactions. The temperature coefficient of 1·5 per 10° rise is high for photochemical processes, but this value follows from the mechanism of the reaction put forward by Bodenstein and Lütkemeyer.

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[1] See Lewis, *J. Chem. Soc.*, **105**, 1914 *et seq.*

[2] Kastle and Beatty, *Amer. Chem. J.*, 1898, **20**, 159; Pusch, *Zeitsch. Elektrochem.*, **1918**, **24**, 337; Lind, *J. Phys. Chem.*, 1924, **28**, 55; Bodenstein and Lutkemeyer, *Zeitsch. physikal. Chem.*, 1924, **114**, 208.

Photocatalytic oxidation.—In agreement with the Draper Law of Absorption, photochemical halogenation occurs in presence of light from the visible portion of the spectrum. Chlorination is promoted principally by the blue and violet light rays. Many other reactions, however, are catalytically accelerated by the ultra-violet regions of the spectrum, and among such may be included a number of photocatalytic oxidation processes. Of oxidation processes in gaseous systems, attention may be directed to the photochemical acceleration of the oxidation of sulphur dioxide to sulphur trioxide, of hydrogen to water vapour, and of carbon monoxide to carbon dioxide. All these processes have been studied under the influence of the light from the electric arc or the mercury vapour lamp.

From the point of view of reaction kinetics, little has resulted, as yet, from such investigations, in large measure owing, doubtless, to the difficulties of experimental technique. The evidence points to the action of a catalytic agent resulting from the action of light on the oxygen. In the investigation of the oxidation of sulphur dioxide by Coehn and Becker[1] the main feature of the results obtained is the photochemical equilibrium set up. It was found that with the gases in stoichiometric proportions the equilibrium attained, over a temperature range of 50°-800°, was constant and corresponded with an SO_3 content of 65 per cent. With variation of the concentrations of the reacting substances, varying equilibria were obtained corresponding with those demanded by the law of mass action. The precise explanation of this feature is still wanting, and awaits, doubtless, the formulation of the reaction mechanism.

The combination of hydrogen and oxygen under the influence of ultra-violet light, studied by Andreew,[2] was shown to be a reaction independent of the concentration of the reacting gases. Coehn and Grote,[3] on the other hand, claim that it is a reaction of the first order. In reality there is, probably, no discrepancy between these two results, since Andreew worked with a mixture of the two gases alone, whilst the observations of Coehn and Grote were carried out with the minimal quantities of the two gases present near the equilibrium state of the system. The order of reaction is governed by the degree of absorption of the active rays, and, in the simple hydrogen-oxygen mixture, if this were complete, a reaction of the zero order would result, in which the reaction velocity is independent of the concentrations of the reacting substances

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[1] *Zeitsch. physikal. Chem.*, 1910, **70**, 88.

[2] *J. Russ. Phys. Chem. Ges.*, 1911, **43**, 1342.

[3] *Nernst Festschrift*, Halle, 1912, p. 136.

Definite information as to the function of the various substances present in such oxidation processes emerges from the interesting research of Chapman, Chadwick, and Ramsbottom[1] on the oxidation of carbon monoxide It was definitely shown in this work that ozone was simultaneously produced, and that, moreover, carbon monoxide acted as an inhibitor of ozone decomposition For, whereas, under the experimental conditions employed, pure dry oxygen yielded only 3·5 per cent of ozone, it was found that when dry carbon monoxide was present the ozone concentration rose to as much as 19 per cent, with simultaneous formation of but 10 per cent of carbon dioxide Further, it was, shown that water acted either as an accelerator of ozone decomposition or as a promoter of the oxidation of carbon monoxide , for, if the gases were saturated with water vapour at the ordinary temperature only 1 per cent of ozone was produced with the same illumination as that cited in the case of the dry gases, whilst, simultaneously, as much as 28 per cent of carbon dioxide was produced

Of oxidation processes in liquid system, the oxidation of hydriodic acid may be cited Since this reaction has been employed for actinometric purposes, it has been frequently studied and most thoroughly by Plotnikow[2] The process is, in reality, the oxidation of the iodide ion in acid solution by atmospheric oxygen, a reaction which, as is well known, takes place slowly in the dark , much more rapidly, however, when illuminated Plotnikow showed that the photochemically active rays (the blue and violet of the mercury arc) were but feebly absorbed by the reacting system Obviously, therefore, the reaction must be exceedingly light-sensitive, which fact also emerges from a computation of Bodenstein that 10^{10} molecules of oxygen react per quantum of light energy absorbed Winther[3] has recently studied this reaction in the dark and in light of wave-lengths 4360, 4050, 3660, 3130, 2800, and 2540 Å The now familiar influence of impurities or added substances on the velocity of reaction is in this case also marked The nature and concentration of the acid employed determine the reaction velocity Certain added substances, as, for example, quinine, accelerate the reaction largely , others act inhibitively Bodenstein has suggested an interpretation of the experimental results, assuming activation of oxygen by electrons set free from the hydriodic acid or accelerators present in the system Weigert suggests the mechanism of reaction nuclei on which the oxygen is condensed at a higher reacting potential He points to the proved existence of peroxide compounds in several of the investigated cases of photochemical oxidation Thus Richardson[4] was able to demonstrate the presence of hydrogen peroxide in the photochemical oxidation of oxalic acid, ether, and amyl alcohol.

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[1] *J. Chem Soc* 1907, **91**, 942

[2] *Zeitsch physikal Chem*, 1907, **58**, 214

[3] *Zeitsch physikal Chem*, 1924, **108**, 236

[4] *Ibid*, 1894, **15**, 505, 1897, **22**, 650.

The promotion of peroxide formation by photocatalytic means has attained technical importance in connection with a series of reactions elsewhere discussed in the section on autoxidation. The production of rapid-drying oils by preliminary exposure to light is now a recognised technical process. Illumination evidently promotes the formation of autocatalysts, presumably of the peroxide type, which subsequently accelerate the oxidation and drying of the oil on exposure to air.[1]

The presence of hydrogen peroxide has also been demonstrated by Weigert[2] in the solutions obtained after the photocatalytic oxidation of quinine by means of atmospheric oxygen. This reaction is remarkable in other ways, since, as is obvious from the experimental results obtained, oxygen, although participating in the reaction, also acts as an inhibitor. The product of the reaction velocity and the oxygen concentration was shown to be constant over a considerable range. With complete absorption of light the velocity of action is proportional to the quinine concentration. The reaction is likewise sensitive to foreign additions. Thus, in presence of 0·1 normal sulphuric acid, reaction is completely suppressed.

The oxidation of quinine with chromic acid as oxidising agent was studied in detail by Luther and Forbes.[3] In this case the reaction velocity is determined by the light absorbed by the molecules of quinine. The chromic acid is not the light-sensitive agent. The reaction is not markedly sensitive to impurities, and occurs quite rapidly in high acid concentrations, in marked contrast to the previous case of oxidation by atmospheric oxygen. Luther and Forbes, by a study of the reaction under the influence of varying wave-lengths, were able to demonstrate the influence of absorption on the order of reaction. The violet region of the mercury vapour lamp is only feebly absorbed by quinine. In this region the reaction is unimolecular. At the ultra-violet end of the spectrum the absorption was practically complete and the reaction in that region was of zero order Only at low concentrations has the chromic acid any influence on the reaction velocity, which points, obviously, to the conclusion that by interaction of light and quinine a photocatalyst results, which then reacts with the chromic acid. As is usual with successive reactions of this type, the *tempo* of the whole process is governed by the slowest of the individual reactions, and this in turn is determined by the concentrations of the reacting substances.

Photocatalytic oxidation in presence of chromates as oxidising agents has found extended technical application in photographic and lithographic processes. The application is based on the discovery that substances such as gelatin, glue, fish-glue, albumin, etc., when heated with solutions of chromates, are rendered partially or completely insoluble in water after exposure to light. The degree of insolubility is proportional to the intensity of illumination. In photography, using pigmented gelatin layers, this has led to the beautiful "carbon process" and numerous allied processes. In lithography, employing metallic bases covered with a chromated gelatin layer or layers of similar substances, the permeability to acids is determined by the intensity of illumination. Thus it is possible to obtain etched reliefs from which, by the ordinary printing processes, prints may be obtained. The actual mechanism of the photochemical action on the colloidal material, although the object of considerable investigation, is, as yet, not satisfactorily settled. In its main features it is undoubtedly parallel to the case of quinine just discussed. But the mechanism whereby insolubility is produced is not yet clear.

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[1] See, in this connection, p. 221, and Fahrion, *Chem Zentr.*, 1905, **1**, 305 , Genthe, *Zeitsch. angew. Chem.*, 1906, **19**, 2087 ; 1909, **22**, 2095.

[2] *Nernst Festschrift*, Halle, 1912, p. 464.

[3] *J. Amer. Chem. Soc.*, 1909, **31**, 770.

A photocatalytic process of common everyday observation is the fading of coloured materials and pigments on exposure to light. Whilst possibly not exclusively oxidation processes, it has been shown in many cases that the reactions are autoxidations catalytically accelerated by light. Weigert[1] has shown, for example, that with substances like fluorescein and erythrosin the mechanism is parallel to that observed by him for quinine. Lasareff has, however, demonstrated[2] that in thin colloidal films the bleaching of pigments is due not only to oxidation but also to intramolecular decomposition. Also the complexity of the problem is intensified by the influence of added substances. Thus it has been demonstrated, by observations with the ultramicroscope,[3] that addition of potassium ferrocyanide gives rise to a heterogeneous catalyst, peroxide in nature. The addition of iodine strongly accelerates certain of these reactions, as does also the presence of the ions OH′, NO_3′, ClO_4′. Retardation occurs in presence of $H^{\cdot}$, Cl′, Br′, and SO_4′ ions.

The formation of an autocatalyst, of which the activity persists for long periods after illumination has been discontinued, is well illustrated in the case of the oxidation of iodoform.[4] On bubbling oxygen through illuminated solutions of iodoform in the most diverse solvents, oxidation occurs, with separation of iodine. The velocity of reaction increases with increasing initial concentration of iodoform in degree corresponding with that required in accordance with Beer's Law. The velocity varies with the nature of the solvent. Thus, in carbon tetrachloride solution, the reaction is fourteen times as rapid as in alcohol. The influence of iodine is, however, most marked. For, although in the replacement of iodoform by iodine during the course of the reaction the absorption of light is strongly altered, still the velocity of reaction remains constant. Also, after discontinuance of illumination, the process of oxidation continues steadily for long periods in the dark. If, also, to an unilluminated solution of iodoform in certain solvents a small amount of a pre-illuminated solution be added, oxidation takes place without any further illumination. Obviously, illumination gives rise to a photocatalyst which persists in activity over long intervals. The phenomenon is not definitely explained. The process is undoubtedly complex and presumably is quite different in different solvents, since only in certain solvents is the activity, on discontinuance of illumination, observable.

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[1] *Loc. cit.* [2] *Zeitsch. physikal. Chem.*, 1912, **78**, 657.

[3] See Amanns, *J. Suisse de Chem. et Pharm.*, 1901; Kistiakowski, *Zeitsch. physikal. Chem.*, 1900, **35**, 431.

[4] Szilard, *Zeitsch. wiss. Photochem.*, 1904, **4**, 127; Plotnikow, *Zeitsch. physikal. Chem.*, 1910, **75**, 337, 385.

The inhibition of certain photo-oxidations has already been dealt with in the chapter on the inhibition of homogeneous reactions (pp 151, 155).

Photocatalytic hydrolysis.—The hydrolysis of hydrochloroplatinic acid has been shown by Boll and Jacob[1] to be photochemically sensitive to ultra-violet radiation. The different acids H_2PtCl_6, $H_2PtCl_5(OH)$, $H_2PtCl_4(OH)_2$, and $H_2PtCl_2(OH)_1$ are all hydrolysed by water, the rate of reaction being readily followed with great exactitude by determination of the conductivity of the solution. The formation of hydrochloric acid during the reaction causes an increase of conductivity. With weak absorption the reaction is of the second order; with considerable absorption the velocity is proportional to the chloroplatinic acid concentration. The authors regard this reaction as pointing to the formation of a compound, $H_2PtCl(OH)_5 \cdot H_2Pt(OH)_6$, the production of which is suggested also by a measure of the absolute amount of hydrochloric acid produced. By direct measurement it was shown that, in $\frac{1}{10000}$ normal solution, about two molecules of acid were decomposed per quantum of light energy absorbed. In stronger solutions the number decomposed would probably be proportionately greater. By analogy with the hydrogen-chlorine reaction, Bodenstein suggested that the reaction should be inhibited by oxygen. Boll and Henri, however,[2] on submitting this point to experimental test, could not confirm this suggestion, and consequently doubt was cast on the whole systematisation introduced by Bodenstein.

From the quantitative point of view, the mechanism of numerous photochemical reactions has been studied by Henri and his co-workers. Of the reactions included under hydrolysis, that of acetone may be cited. Henri and Wurmser[3] showed that the reaction was photochemically quite sensitive, the ratio of molecules hydrolysed to quanta absorbed being in the ratio of 200 to 1. Baly[4] suggests, however, in regard to this result, that a portion of the necessary energy for the reaction is derived from the solvent, which exerts, according to this view, an influence in opening up the electrical fields of force of the solute molecules Of interest also from the same work of Henri and Wurmser is the observation that the minimum of energy capable of producing luminous sensation in the eye is inferior to the elementary quantum of energy

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[1] *Compt. rend.*, 1912, **154**, 881; 1912, **155**, 826, 1913, **156**, 138, 691.

[2] *Compt. rend.*, 1914, **158**, 32.

[3] *Ibid.*, 1913, **156**, 1012.

[4] *Physikal. Zeitsch.*, 1913, **14**, 893.

Photocatalytic decomposition and polymerisation.—Typical examples of decomposition photochemically accelerated are the decomposition of ozone and hydrogen peroxide, together with the decomposition of oxalic acid in presence of uranyl salts All three reactions have been the object of a considerable amount of experimental work, from which certain conclusions relative to the reactions may be drawn

Thus, in the decomposition of ozone, it was shown by Regener[1] that ultra-violet light in the region of 0 257μ was particularly active The kinetics of the reaction has been studied, more especially by von Bahr[2] and by Weigert[3] With complete absorption of light, reaction is proportional to the ozone concentration With homogeneous illumination—that is, with extremely thin gas layers the reaction would be proportional to the square of the ozone concentration, which is in part made manifest in the available experimental data From Weigert's data it may be calculated that, in his experiments, approximately 100 molecules of ozone are decomposed per quantum of energy absorbed

It was thought that, in visible light, ozone was stable, recent investigations by Griffith and Shutt,[4] initiated as a result of calculations made by Lewis[5] in 1918 on the basis of the radiation theory of chemical action, have served to show that ozone may be decomposed by visible light of wave-length longer than 6700 Å and, therefore, in the red region of the visible spectrum This prediction by Lewis and subsequent verification by Griffith and Shutt constitutes one of the positive achievements of the radiation theory

As regards the sensitisation to visible light by the addition of chlorine, Weigert showed,[6] in an intensive investigation, the far-reaching proportionality between light absorbed and ozone decomposition, independent of the ozone concentration within wide limits An estimate of the photochemical yield by Bodenstein[7] showed the ratio of absorbing to reacting molecules to be of the order of unity

The sensitised reaction has been recently studied by Bonhoeffer[8] from the standpoint of the quantum relationship and the law of the photochemical equivalent, using approximately monochromatic illumination ($\lambda = 4360$ Å and a group at 4060 Å), measuring, with every refinement, the energy involved and chemical reaction produced

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[1] *Ann Physik*, 1906 (iv), **20** 1033

[2] *Ibid*, 1910 (iv), **33**, 598

[3] *Zeitsch physikal Chem*, 1912, **80**, 78

[4] *J Chem Soc*, 1921, **119**, 1948

[5] *Trans Farad Soc*, 1922, **17**, 579

[6] *Zeitsch Elektrochem*, 1908, **14**, 591

[7] *Ibid*, 1913, **19**, 840

[8] *Zeitsch physikal Chem*, 1923, **13**, 94

Chlorine and bromine were used as sensitisers. It was shown that, with chlorine, the rate of reaction was strictly proportional to the absorbed light, independent of the ozone concentration between concentrations of 5 and 0·1 per cent. The velocities with monochromatic radiation were, naturally, considerably less than in Weigert's studies with a whole spectral region.

Bonhoeffer's results show that about two molecules of ozone were decomposed for each quantum absorbed. With bromine vapour as sensitiser the reaction was more difficult to study. The dark reaction amounted to 10-20 per cent of the sensitised reaction The remarkable result of the quantitative investigation can be gathered from the observation that, in four different experiments, the values for $N/h\nu$ were 34·5, 28·2, 33·2, and 28·2, or, in the mean, 31. No simple ratio exists, therefore, in the bromine sensitised reaction, between absorbing and reacting molecules.

In his discussion of the experimental results Bonhoeffer stresses the remarkable nature of the observation that the reaction velocity is independent of ozone concentration within the limits 5–0·1 per cent. This points to a remarkable "life" of the activated chlorine molecule, since, in the more dilute ozone mixture, such a molecule must meet 1000 molecules of chlorine and oxygen before it reaches an ozone molecule. This would cast doubts on the mechanism postulated, in the hydrogen-chlorine combination, for the inhibitory power of oxygen. From kinetic data Bonhoeffer calculates a minimum life of $1{\cdot}6 \times 10^{-7}$ secs. That two molecules of ozone are decomposed is in agreement with data on the photosensitivity of ozone itself

That, in the case of bromine sensitisation, more than thirty ozone molecules decompose for every activated bromine molecule compels us, in the view of Nernst and Noddack,[1] to assume that energy must be transferred from activated ozone molecules to inactivated, or that the energy of the reaction products may be so transferred.

His own earlier data and the confirmatory data of Bonhoeffer have led Weigert to a detailed consideration[2] of the theory of the transformation of radiation. Weigert sees in the ozone-chlorine sensitised reaction the simplest case of chlorine photoreactions, and he would therefore expect to draw from the reaction the simplest conclusions as to mechanism. He points to the importance of the fact that the velocity of reaction is independent of the ozone concentration at a certain, but small, ozone concentration, as showing that, at and above this concentration, all or practically all the radiant energy absorbed by the chlorine is converted into chemical energy. Similar observations have been made by Gruss[5] for two sensitised reactions involving trichlorbrommethane:

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[1] *Sitzungsber. preuss. Akad.*, 1923, 113

[2] *Zeitsch. physikal. Chem.*, 1923, **106**, 403

[3] *Zeitsch. Elektrochem.*, 1923, **29**, 144.

$$2CCl_3Br + Cl_2 = 2CCl_4 + Br_2,$$

$$2CCl_3Br + O_2 = 2COCl_2 + Br_2 + Cl_2$$

With chlorine free from ozone, but containing moisture or other impurities in small quantities, light may be absorbed and converted completely into heat energy, as shown by chlorine in the Budde effect,[1] the expansion due to temperature rise when moist chlorine is illuminated.

Weigert sees a complete analogy to these two modes of transformation of light energy in experiments with mercury vapour. In pure mercury vapour at low pressures Wood[2] showed that the resonance line, 2536 Å, can readily be stimulated by illumination with a mercury vapour lamp. By addition of air or other gases this resonance radiation can be suppressed entirely. In this event Wood says that a true absorption occurs, the light energy introduced being converted into heat. Now, it has recently been shown by Cario and Franck[3] that the light energy can be transformed into chemical energy if the gas added to the mercury vapour is hydrogen. These authors showed that an illuminated system of mercury vapour and hydrogen decreased in pressure, owing to the production of hydrogen atoms which "cleaned up"[4] on the walls of the containing vessel or could reduce copper oxide at ordinary temperatures. According to Cario and Franck there exists also, in this case, a limiting hydrogen pressure above which all the absorbed light energy is converted into chemical energy.

The limiting pressures of the reacting species, of ozone at 0·5 mm. or lower and of hydrogen at 10 mm. Hg pressure, and the pressures of the sensitising agents (chlorine, 0·5 atom., and mercury, 0·009 mm.) are quite different. The ratio of reacting to sensitising molecules is also different: for the ozone-chlorine reaction, $n_r/n_s = 1{\cdot}3 \times 10^{-3}$, and for the mercury-hydrogen, $1{\cdot}1 \times 10^3$. If, however, Weigert points out, one calculates the number of reacting molecules which are to be found in photochemically comparable volumes of a cylindrical vessel, corresponding to the thickness through which the absorbed radiation is reduced to the same extent, practically identical numbers are obtained in the two cases. This occurs by reason of the strong absorption of mercury vapour and the small absorption of chlorine. Weigert therefore thinks it probable that the processes are quite analogous to one another.

The weakness of Bonhoeffer's concept of a long-lived chlorine molecule, unable to lose its energy to oxygen or other chlorines but only to ozone when chemical reaction ensues, is evident when the mercury cases are considered. Under given conditions, all three types of phenomena, resonance radiation, heat, and chemical reaction, can result from one and the same primary photo-process, the absorption of light from the mercury vapour lamp. Weigert, therefore, assumes that in the ozone-chlorine reaction the same process occurs as in the mercury reactions. The radiation absorbed by the chlorine is first emitted as isochromatic resonance radiation in the normal way. and this absorption and emission process is repeated continuously by the chlorine until, finally, absorption in a binary system (involving ozone simultaneously) leads to an inner photo-electric effect and to chemical change or to a change in translatory energy of the particles.

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[1] *Pogg. Ann.*, 1871, **144**, 213; *Ergbd.*, 1873, **6**, 477.

[2] *Phil. Mag.*, 1909, **18**, 187; *Physikal. Zeitsch.*, 1909, **10**, 425.

[3] *Zeitsch. Physik*, 1922, **12**, 162.

[4] Langmuir, *J. Amer. Chem. Soc.*, 1914, **36**, 1710; 1915, **37**, 417; 1916, **38**, 1145.

The resonance radiation of the mercury can be perceived because of the extraordinarily strong absorption of the exciting light; with chlorine it is imperceptible because the absorption is a hundred million times smaller. On the other hand, there is indirect evidence of its occurrence. For the Budde effect only occurs with moist chlorine or chlorine containing small impurities. With pure dry chlorine, no Budde effect is observed, although absorption occurs. Weigert assumes that, in this case, the absorbed energy is re-emitted as isochromatic resonance radiation.

This mechanism of Weigert is in agreement with his observation that perceptible time intervals occur during which the observed chemical change is completed It does not explain abnormal yields of chemical energy. To explain such, some type of chain mechanism or of energy transference from products to reactants must be assumed.

Catalytic effects in ozone decomposition. Various gases have been found to accelerate ozone decomposition; optical sensitisation cannot be the cause of the acceleration observed, since the gases do not absorb the wave-lengths employed. Weigert[1] and Weigert and Bohm[2] have studied the decomposition of ozone by ultra-violet light in the presence of hydrogen. Pronounced acceleration is produced. Griffith and Shutt[3] have studied the same system in visible light, and Griffith and MacWillie[4] have studied the reaction in the presence of helium, argon, nitrogen, carbon monoxide, and carbon dioxide.

Weigert assumes that the decomposition of ozone in the presence of hydrogen is not a photochemical process but a thermal reaction. The heat liberated by the reaction

$$O_3[b] + H_2 = O_2 + H_2O$$

is supposed to warm the gas in the neighbourhood of the absorbing layer to a temperature high enough to enable the bimolecular thermal reaction

$$2O_3 = 3O_2$$

to proceed at an appreciable rate. Griffith and Shutt reject this mechanism for visible light, since there is no greater increase in temperature on illumination of gas mixtures containing hydrogen than in those containing ozone and oxygen alone. Griffith and Shutt suggest that the water molecules formed, which, for some period after their formation can possess energy, can activate ozone molecules by collision In the absence of hydrogen the ozone decomposition is much slower and is bimolecular, in agreement with the ultra-violet reaction with weak absorption

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[1] *Ber.*, 1913, **46**, 815.

[2] *Zeitsch. physikal. Chem.*, 1915, **90**, 194, 233.

[3] *J. Chem. Soc.*, 1923, **123**, 2752.

[4] *J. Chem. Soc.*, 1923, **123**, 2767.

With carbon monoxide present in the ozone mixture, reactions similar to those with hydrogen can occur With the other gases present, only the ozone decomposition

$$2O_3 = 3O_2$$

occurs, the velocity being greatest with helium admixed, less so in order with argon, nitrogen, and carbon dioxide, least of all with oxygen-ozone mixtures alone, comparisons being made at the same ozone concentration Were the admixed gases acting as diluents to an inhibitory oxygen concentration the specific order given would not be anticipated -they would all be expected to have a like action Griffith and MacWillie therefore suggest that the order of efficiency is an index of the efficiency of the admixed gas in causing deactivation of the ozone molecules by collision[1]

In connection with the decomposition of hydrogen peroxide under illumination, it was demonstrated by Kistiakowski[2] that by addition of red and yellow prussiate of potash the catalytic action of light was prolonged for considerable periods after illumination had ceased Ultramicroscopic investigations showed that this could probably be attributed to formation of a heterogeneous catalyst More recently it has been shown that other substances may act in the reverse direction These have already been discussed in an earlier chapter (pp 152, 153) As to the kinetics of the decomposition, Tian[3] reports that in dilute solution the reaction is of the first order More recently,[4] however, he published figures which point to the fact that the decomposition is proportional to the light absorbed and the concentration of peroxide, and that the oxygen evolved in the reaction acts as an autocatalytic inhibitor Henri and Wurmser[5] report but feeble absorption of the light energy and a decomposition of more than 100 molecules per quantum absorbed

The decomposition of oxalic acid in presence of uranyl nitrate is very sensitive to light Between the concentration limits of $N/1000$ and $N/10{,}000$ the velocity is strictly proportional to the absorbed energy,[6] and 500 molecules of acid are decomposed per quantum of energy absorbed The hypothesis of Bodenstein that oxygen would act as inhibitor of this reaction was also shown by Henri and Boll[7] to be in disagreement with experimental facts The reaction has also been studied by Mathews and Dewey,[8] and quite recently by Anderson and Robinson,[9] who show that the system oxalic acid-uranyl sulphate-water forms a suitable ultra-violet radiometer. They find, however, that many quanta are required per molecule decomposed, the number decreasing with increase of uranyl sulphate concentration.

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[1] See also G B Kistiakowski, *Zeitsch physikal Chem* , 1925, **117** 337

[2] *J Chem Soc* , 1901, **35**, 431 [3] *Compt rend* , 1910, **151**, 1040 [4] *Ibid* , 1913, **156**, 1879.

[5] *Ibid* , 1012 [6] Boll, *ibid* , 1913, **156**, 1891 [7] *Ibid* , 1914, **158**, 32

[8] *J Physical Chem* , 1913, **17**, 216 [9] *J Amer Chem Soc.*, 1925, **47**, 718

The photochemical acceleration of processes of polymerisation may be exemplified in the researches of Berthelot and Gaudechon[1] on acetaldehyde. In presence of moisture and oxygen, acetaldehyde is rapidly oxidised by ultra-violet light to acetic acid. Even in absence of oxygen, with the extreme rays of ultra-violet light, oxidation sets in, presumably with simultaneous decomposition. In absence of moisture, and most rapidly in the vapour phase, acetaldehyde resinifies and forms polymerised products on illumination with rays of wave-length less than 0·25μ.

CATALYSIS BY MEANS OF RÖNTGEN RAYS, THE SILENT DISCHARGE, AND RADIOACTIVE SUBSTANCES

In the preceding sections of this chapter it has emerged that light energy may promote widely diverse and distinct catalytic reactions. In most cases, from lack of full investigation, it has been impossible to determine the actual *modus operandi*, but it is obvious that in many cases the function of the light energy absorbed has been the production of a catalytic agent which has accelerated the operation of a reaction in the normal direction of the chemical forces. It would be expected, therefore, that in the operation of other forms of radiant energy on chemical systems similar catalytic effects would be observed. Thus an examination of the material available concerning the influence of the silent electric discharge, of Röntgen rays, and of the radiations emitted during radioactive transformations, should reveal examples parallel to those cited in the sections dealing with photochemical changes.

The literature of chemical reactions induced by these different types of radiation is scanty, however, doubtless due to the recent date of their discovery and elucidation. In the main the literature deals with reactions which cannot be included in the scope of this study, since they are chiefly non-catalytic and in which the reaction occurring is in the direction opposed to the normal chemical forces of the system, deriving the necessary energy from the radiant energy supplied. Thus in the case of the silent electric discharge the formation of ozone from oxygen is an excellent example. As Krüger has already shown,[2] the number of ozone molecules formed is determined by the number of oxygen molecules which are ruptured by the electrons introduced into the gas system.

The decomposition of dry ammonia gas under the influence of the silent discharge is another case parallel to the ozonisation of oxygen. Curiously, however, as was shown by Le Blanc and Davies,[3] addition of nitrogen to the ammonia accelerates the decomposition considerably, whereas hydrogen diminishes reaction. These influences are worthy of more extended investigation.

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[1] *J. Amer. Chem. Soc.*, 1913, **156**, 233.

[2] *Nernst Festschrift*, Halle, 1912.

[3] *Zeitsch. Elektrochem.*, 1908, **14**, 361.

The researches of Fassbender[1] demonstrated the catalytic influence of the silent discharge in the combination of carbon monoxide and oxygen and of hydrogen and chlorine. The alternating field required is much more powerful in the former case, as would be anticipated from the photochemical results. Doubtless, investigation of the latter case would show that as regards kinetics and energy consumption it was parallel to that observed under the influence of light, Rontgen rays, and alpha-particles, which latter will subsequently be detailed.

The function of Rontgen rays in promoting a reaction catalytically is best exemplified in the case of the hydrogen-chlorine combination as studied by Le Blanc and Vollmer[2]. It was found that in a hydrogen-chlorine mixture which was photochemically quite sensitive, Rontgen rays also produced combination. Moreover, in evaluating the ratio of energy supplied to the amount of chemical combination produced, it was shown that 10^4 molecules of chlorine combined for each electron produced in the system by the radiation. The kinetics of the reaction was not studied and remains therefore an interesting problem for comparison with the effect of light energy and of the action of alpha-particles on the same reaction.

A number of qualitative tests on certain reactions, as, for example, the hydrolysis of acetone catalytically accelerated by light, have been made, by one of the authors, with Rontgen rays from a Coolidge tube, but without significant result. That a search for such reactions need not be fruitless, however, is to be concluded from the recent observations of Bordier[3] on the decolorisation of aqueous solutions of iodine and of starch iodide by exposure to Rontgen rays for a few minutes. The quantity of radiation required varied with the proportion of iodine in the solution. Further investigation would doubtless reveal the high catalytic activity of the rays in this particular reaction, and data on the energy quantities involved should be interesting.

Van 't Hoff[4] forecasted the possibility of using radioactive transformations and the energy resulting therefrom as catalytic agents. In evidence of his belief, he directed attention to the action of radioactive materials on the glass vessels in which they were contained. Especially with glasses containing manganese or lead, the coloration produced in the glass by action of the rays evidences an acceleration of a reaction, presumably oxidation, which ordinarily takes place but slowly, being manifested in glass of manganese content by the development of a pinkish tinge.

The reactions brought about by radiations from radioactive substances have been collected and discussed by Lind.[1] The reactions investigated are numerous and include, among others, the formation and decomposition of water, of ammonia, of hydrogen chloride and bromide, the decomposition of carbon monoxide and dioxide, and the ozonisation of oxygen. From a review of the available material Lind was able to establish a definite relationship between the number of molecules brought to reaction and the pairs of ions formed for example, by the alpha-particles introduced into the system. Thus, in the case of ozonisation of oxygen, most carefully and thoroughly investigated by Lind, it was shown that, for every pair of ions, one molecule was caused to react. The reactions may therefore be regarded as due to the direct intervention of the alpha-particles, the energy from which is transformed in the process of the chemical reaction.

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[1] *Zeitsch physikal Chem*, 1908, **62**, 743

[2] *Zeitsch Elektrochem*, 1914, **20**, 494

[3] *Compt rend*, 1916, **163**, 291

[4] *Zeitsch Elektrochem*, 1903, **9**, 736.

The conspicuous exception to the simple relation thus formulated by Lind for the reactions brought about by radioactive energy is again to be found in the case of the hydrogen-chlorine combination. Lind calculated, from experiments of Jorissen and Ringer,[2] that, from one pair of ions, the number of chlorine molecules brought into reaction was of the order 10^2-10^3, similar in magnitude to that observed by Le Blanc and Vollmer for the action of Röntgen rays, and paralleled also by the previously cited computations for the photochemical reaction. The experiments of Jorissen and Ringer were carried out with the gases in an actinometer having a suitable scale attachment, radium salt being contained in a thin-walled tube fitted into the reaction vessel. Evidence for an induction period is manifest from the experimental results as well as for a varying sensitivity of the reacting gases, due, doubtless, to impurities present in the gases.

The analogy between the photochemical reaction and that induced by the alpha-particles is still further emphasised by a study of the reaction by Taylor.[3] The experimental conditions were so arranged that complete absorption of the alpha-particles from radium emanation in a minute, thin-walled glass bulb was effected in the hydrogen-chlorine mixture surrounding the bulb and contained in a spherical reaction vessel of radius greater than the range of the alpha-particles (Fig. 25). In these circumstances of complete energy absorption, it was shown that the reaction velocity was proportional to the energy absorbed and was of the first order, inversely proportional, however, to the total pressure, which changed during an experiment by withdrawal of samples for analysis. These results could be interpreted by a reaction equation of the form

$$\frac{d2\mathrm{HCl}}{dt} = R\frac{E_{\mathrm{abs}} \times [\mathrm{Cl}_2]}{[\mathrm{O}_2]},$$

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[1] *J. Physical Chem.*, 1912, **16**, 564, "Chemical Effects of Alpha Particles and Electrons", Chem. Catalog Co.

[2] *Ber. Chem. Ges.*, 1906, **39**, 2065.

[3] Taylor, *J. Amer. Chem. Soc.*, 1915, **37**, 24; 1916, **38**, 280.

which, for small energy absorption such as holds in the photochemical reaction, would change to the square of the chlorine concentration and yield; therefore, a reaction equation identical with that obtained by Bodenstein and Dux in the photochemical reaction On the energy side it was computed that, with the most reactive gas mixture employed — which, however, was considerably less sensitive, photochemically, than the gases of Bodenstein and Dux—as many as 2×10^4 molecules of chlorine reacted for every pair of ions introduced into the reaction space, thus confirming the calculation of Lind relative to Jorissen and Ringer's work and establishing conclusively the catalytic influence of the alpha-particles in the reaction

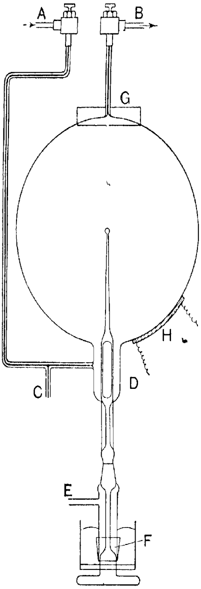

FIG. 25—*A*, gas inlet, *B*, gas outlet, *C*, manometer connection, *D*, silica rod as compensator for thermal expansion of mercury, *E*, inlet for emanation, *F*, mercury scale, *G*, ice reservoir, *H*, electric heater, to ensure rotation of gases

Extension of the work on the action of alpha-particles by Lind and Bardwell[1] to the oxidation of aliphatic hydrocarbons, the polymerisation of acetylene, cyanogen, and hydrogen cyanide has revealed a new type of gaseous catalysis The polymerisation of acetylene yields a yellow solid polymer, obtained by Sabatier by the action of copper on acetylene and called by him "cuprene" This polymerisation, under the influence of alpha-particles, differs from the normal results obtained with alpha-particles in that as many as 20 molecules of acetylene polymerise per pair of ions produced This is ascribed by Lind and Bardwell to the formation of a "cluster" of twenty acetylene molecules around a single ion, the polymerisation occurring within the cluster. These authors have also found that the ions of "inert" gases can also act as clustering centres Thus, nitrogen, helium, neon, and argon ions have the same power of causing the polymerisation of acetylene as the ion of the gas itself. Since these gases do not enter into permanent combination, Lind and Bardwell term the effect "ionic catalysis".

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[1] *Science*, 1925, **62**, 422, 593

This type of catalysis is not confined to polymerisation processes of the type mentioned. It was shown that nitrogen ions contribute as much as do the O_2^+, H_2^+, and O_2^- ions to the reaction velocity of hydrogen-oxygen combination. Since the ionisation of nitrogen is almost double that of electrolytic gas, when they are mixed in equal proportion, $1N_2$ to $1(2H_2 + O_2)$, the reaction rate would be expected to be nearly three times as fast as if nitrogen were absent, which was found experimentally to be the case. Argon when mixed with electrolytic gas was also found to have a positive catalytic effect, though less than that of nitrogen. Carbon dioxide acts normally as an inert ion catalyst in the polymerisation of acetylene. In the oxidation of carbon monoxide to carbon dioxide, the reaction product, however, appears to have no such catalytic effect, although argon acts as an ion catalyst in this same reaction. The reason for the failure of carbon dioxide to act as an ion catalyst for its own production from carbon monoxide and oxygen is, therefore, not yet clear. Further work in this class of catalysis is therefore promised.

The polymerisation of acetylene to form "cuprene" can also be produced by Lenard rays from the X-ray tube. If these high-speed electrons be driven under high voltage through metal windows in the X-ray tube into an atmosphere of acetylene, a copious production of "cuprene" results.[1] As yet, no quantitative data are available. It has been shown, however, that the same source of energy will cause hydrogen and chlorine to explode, hydrogen and oxygen to combine, as is the case, also, with the beta-particles from radium.

[1] Coolidge, *Science*, 1926.

CHAPTER XVII

CATALYSIS IN ANALYTICAL CHEMISTRY

THE recognition of the applicability of catalytic operations to the purposes of analytical chemistry dates from the earliest days of the investigation of catalysis Dobereiner's experiments on the combustibility of oxygen-hydrogen mixtures in presence of platinum wire and Sir Humphry Davy's parallel researches on the ignition of coal gas-oxygen mixtures by means of fine platinum wires introduced into them at a temperature below the ignition point, were both of especial and recognisable significance in the problem of the analysis of gaseous mixtures Indeed, already in 1821, Turner, in a communication to the Royal Society of Edinburgh, published in the Edinburgh *Philosophical Journal*,[1] had discussed the experiments of Dobereiner and of the possible extension of his method to the promotion of combination between other gases such as hydrogen and chlorine or iodine Turner, moreover, envisaged the possibility of a separation of gases by means of fractional combustion, but was unsuccessful in his attempts Immediately afterwards, the studies of W Henry[2] demonstrated the use of platinum in fractional combustion in a series of researches still of remarkable and fundamental import to the student of catalytic processes

In a similar manner, the catalytic reactions were exploited in the direction of analytical application, either qualitative or quantitative The discovery of the efficacy of platinum as oxygen carrier found manifold developments Thus, Dobereiner's demonstration of the oxidation of alcohol to acetic acid in presence of platinum or iridium sponge[3] was later applied as test for alcohol[4] Rose,[5] recognising the accelerating action of platinum on the combustion of organic substances, recommends the addition of platinum black in the determination of ash in combustible matter, the principle being later extended to other contact substances—for example, ferric oxide[6] and silver.[7]

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[1] 1824, **11**, 99, 311 [2] *Phil Mag*, 1825, **65**, 269 [3] *Schweigger's J*, 1831 (iii), **63**, 476

[4] Carstanjen, *Jacobsen's Chem Techn Report*, 1863, **2**, 92

[5] *Hand d anal chem*, 1851, **2**, 775

[6] Graeger, *Ann Chim*, 1859, **111**, 124, Mullen, *J pr Chem*, 1860, **80**, 118

[7] Kastner, *Zeitsch angew Chem*, 1889, **2**, 205

Copper and its compounds were early recognised for their catalytic properties, and found application in analytical operations, chiefly in gas analysis, organic analysis, and as accelerators for solution processes. Thus, Williams utilised the copper-zinc couple[1] for reduction and estimation of nitrates. The siccative action of metallic lead, discovered by Chevreul,[2] was the forerunner of the numerous analytical methods for the determination of the oxidation of drying oils. The decomposition of hydrogen peroxides by finely divided platinum metals, another of the catalytic reactions already known in the Berzelius period of activity in matters catalytic, was also applied later to the gas volumetric determination of the peroxide,[3] especially in solutions containing organic substances.

With the application, however, of the concept of reaction velocity to a study of catalytically accelerated reactions, immense impetus was given to the analytical application of catalysis, both in its qualitative and quantitative aspects. The scope of the investigator was gradually extended by a variety of new catalytic reactions, with which it was possible to demonstrate the presence and amount of acids and bases, and salts such as iodides. This development led naturally to a more fundamental and far-reaching study of the catalytic reactions, the influence of concentration, of non-essential materials which were present, of the retardation or negative catalysis that might occur, as well as to the mechanism whereby the acceleration of the reaction occurred. All of which has contributed to a very copious literature which it would be impossible, even in the scope of the whole of the present volume, to record and detail. It seems apposite, however, to outline the various broad developments of the application of catalysis to analytical chemistry and to do so in sections dealing respectively with catalysis in gas analysis, in inorganic and in organic analysis, both qualitative and quantitative, as well as in the applications of physico-chemical measurements.

CATALYSIS IN GAS ANALYSIS

Analytical combustion processes.—The analysis of combustible gases by catalytic means is a matter of the utmost simplicity, when such combustible gases are present singly in a given mixture. Thus hydrogen, in mixtures of non-combustible gases containing oxygen, may be estimated by combustion in the presence of finely divided palladium or palladised asbestos even at the ordinary temperature, though naturally the velocity is usually accelerated by raising the temperature. This constitutes the modification by Lunge and by Hempel of the original investigations of Turner, previously cited, in which researches it was shown that with the aid of platinum balls (mixtures of clay and platinum) quite minute quantities of hydrogen or of oxygen in mixtures of the two could readily be determined, even in mixtures the concentrations of which were such that explosion methods were not available. The composition of the gas is readily deducible from the observed contraction.

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[1] *Analyst*, 1881, 6, 36.

[2] *Traité des corps gras*, 1823.

[3] Ebell, *Zeitsch. d. Vereins Deutsch. Ing.*, 1881, p. 26.

In a similar manner, carbon monoxide may be determined by combustion with excess of oxygen in a heated capillary tube containing palladised asbestos, the percentage being determined in the absence of other combustibles by the contraction in volume observed after passage over the catalyst. In presence of hydrogen, the quantity of carbon monoxide consumed is readily obtained by absorption in alkalis of the carbon dioxide produced. The method in the case of both hydrogen and carbon monoxide is by no means restricted to the use of the platinum metals as catalytic agents, although these have mainly been employed in actual analytical practice. For, it can readily be shown that many other agencies will effect the catalytic combustion of hydrogen or carbon monoxide. Thus copper oxide, when suitably prepared by alternate reduction and oxidation at low temperatures, will readily catalyse the combustion mixtures of these gases and oxygen or air at temperatures below 200°. Jones and Taylor[1] have shown that small quantities of oxygen in carbon monoxide may be quantitatively converted to carbon dioxide in presence of active reduced copper even at 0° C. Finely divided nickel is an extremely efficient catalyst for combustion of hydrogen and oxygen at comparatively low temperatures. Ignited bog-iron ore has also been employed for low-temperature combustion of carbon monoxide and hydrogen.

Of the hydrocarbons, it was demonstrated by Henry that ethylene, when mixed with sufficient oxygen, began to burn in contact with platinum sponge at 250°, and was completely oxidised at 270°. He further found that methane began to oxidise at temperatures just above 290°. This observation, however, is in sharp contrast to the results of Richardt,[2] who found no combustion at 450°, and negligible combustion in a rapid stream of methane-air mixture through a palladium tube even at 600°-650°. Coquillon[3] applied the method to the determination of methane in the air of coal-mines, using electrically heated glowing platinum or palladium. The method was developed by Winkler[4] and by Dennis[5] with a view to avoiding combustion of nitrogen at the high temperatures attained by the platinum spirals during combustion. The same reaction was made use of by Liveing[6] in an effort to determine methane in suspected mine gas by comparison of the light intensities of two identical spirals heated by the same current—the one burning in air, the other in the mine gas.

Normally, the sulphur-containing gases present in illuminating and fuel gases are determined by a catalytic reduction process.[1] Their estimation, however, by a catalytic combustion process was worked out by Valentin,[2] who passed the gases admixed with air over platinum sponge heated to redness in a porcelain tube, the oxides of sulphur, both di- and trioxide, being collected in absorption liquids, completely oxidised to sulphate, and then estimated. Various modifications of this procedure have been suggested.

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[1] *J. Physical Chem.*, 1923, **27**, 623.

[2] *J. f. Gasbeleucht.*, 1904, **47**, 566, 590.

[3] *Compt. rend.*, 1877, **84**, 458.

[4] *Lehr. d. techn. Gasanalyse*, 1901, p. 180.

[5] See Hempel's *Gas Analysis*.

[6] *Phil. Mag.*, 1880 (v.), **9**, 126.

Preferential combustion.—The principal facts upon which the preferential combustion of gases, as employed in gas analysis, are based have been already given in the preceding section. It is to Henry[3] that we owe the first fundamental investigations of the subject, and upon his methods are based the modern developments of the processes of preferential combustion, more especially as worked out by Hempel.[4] As, normally, absorption methods are used to eliminate such gases as carbon monoxide and the unsaturated hydrocarbons from the mixtures to be analysed, the main use of preferential combustion is in the analysis of mixtures of hydrogen and methane. For this purpose Hempel substituted palladium for the platinum employed by Henry, and it was shown that at temperatures not greater than 100° the hydrogen could be burned without the simultaneous oxidation of any methane. Care must be exercised, however, that the reaction does not become so energetic as to cause local overheating, since, already at 200°, methane starts to react with oxygen. With natural gas the methane is associated with ethane and occasionally even higher homologues. Fractional combustion, using palladium, is here also applicable; the alternative method of Richardt,[5] using a heated palladium wire at carefully controlled temperatures, gave less favourable results.

Copper oxide at 250° will oxidise hydrogen preferentially, methane being completely unattacked,[6] and this method is frequently recommended, as it does not involve the addition of oxygen, and, in the subsequent combustion of methane at a higher temperature, the possibility of simultaneous combustion of nitrogen is eliminated. Obviously, in such circumstances, the reaction is no longer catalytic, but it would doubtless emerge, on examination, that the preferential combustion could be conducted catalytically with copper oxide as contact agent if oxygen or air in excess were added.

In a recent paper[7] Bancroft has given an admirable survey of the problem of preferential combustion, more especially from the viewpoint of selective action of the catalytic agent. As the question is not without considerable interest, not only from the standpoint of analytical chemistry but also from the theoretical point of view and its possible technical applications, it is opportune here to summarise the conclusions reached and to outline briefly the possibilities which they suggest.

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[1] See p. 473.

[2] *Chem. News*, 1868, **17/18**, 89.

[3] *Loc. cit.*

[4] *Ber.*, 1879, **12**, 1006.

[5] *Zeitsch. anorg. Chem.*, 1904, **38**, 65.

[6] Jaeger, *J. f. Gasbeleucht.*, 1898, **41**, 764.

[7] *J. Physical Chem.*, 1917, **21**, 644.

From a résumé of the work of Henry, Bancroft shows that, in contact with platinum, hydrogen burns more readily than ethylene, which in its turn is oxidised before methane This is associated by Bancroft with the absorptive powers of the platinum for the several gases, hydrogen being the most strongly absorbed From the observations of Lunge and Harbeck[1] it is concluded that carbon monoxide is retained most tenaciously by platinum and that in consequence it burns more readily than hydrogen in contact with platinum, which is confirmed by the work of Henry on mixtures of carbon monoxide, hydrogen, and oxygen at temperatures of 150°-170° Henry showed, however, that, when fired by the spark, the preponderance of oxygen was taken by the hydrogen, and not by the carbon monoxide, a result which was later confirmed by Bunsen[2]

Discussing subsequently the researches of Bone and his co-workers,[3] Bancroft points out that the above conclusions are not to be considered anomalous For, Bone succeeded in showing that methane readily oxidises when heated with oxygen in borosilicate bulbs to between 300°-400° at velocities enormously greater than does hydrogen under the same conditions Experiments by Bone on the explosion of methane and hydrogen with quantities of oxygen inadequate for complete oxidation of both gases showed, moreover, that the methane disappeared preferentially in such circumstances In other words, it appeared that methane was oxidised preferentially when burning away from a surface, and that hydrogen disappeared first in contact with agencies such as platinum or copper oxide In other words, the nature of the contact surface determined the order of combustion, which conclusion is rendered more probable from the fact that, contrary to the results with borosilicate glass, hydrogen burns more readily than methane in contact with chamotte at 500°

The influence of the contact agent is further emphasised from the researches of Calvert, who showed[4] that oxygen adsorbed by boxwood charcoal oxidises ethylene to carbon dioxide and water at the ordinary temperature, and, since charcoal has little effect on a mixture of hydrogen and oxygen, it seems probable, according to Bancroft, that charcoal would cause preferential burning of ethylene in a mixture of ethylene and hydrogen The conclusion is therefore reached that by suitable choice of catalytic agent it should be possible to realise all the various alternatives of preferential combustion The extraordinary possibilities which such a conclusion would entail needs but little emphasis in order to be comprehended For it is obvious that, granted a successful result from the search for a suitable catalytic contact agent, many industrial problems might find an easy solution In this connection it may be observed that, in technical practice, there is already one example of preferential combustion in operation, namely, in the removal of sulphuretted hydrogen from illuminating gas, by bog-iron ore absorption with simultaneous revivification *in situ* by addition of air. In this case the hydrogen sulphide is preferentially oxidised at the ordinary temperature to sulphur. Rideal and Taylor[1] applied the principle of preferential combustion of carbon monoxide in hydrogen to the determination of the former gas in large quantities of the latter. A catalyst containing iron, chromium, and cerium oxides was used at a temperature of 250° C. Copper oxide specially activated, or "Hopcalite", a manganese dioxide-copper oxide mixture, can also be used at a temperature of 100° C. The carbon dioxide produced was absorbed in lime-water, or, preferably, in ammonia solutions,[2] and its concentration determined by the change in conductivity of the solution.

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[1] *Zeitsch anorg Chem*, 1898, **16**, 50

[2] *Ges Abh.*, 1904, **2**, 586

[3] *J Chem Soc*, 1902, **81**, 535 *et ff*

[4] *J Chem Soc*, 1867, **20**, 293

Gas analytical reduction processes.—An important application of a catalytic reduction process in analytical work is to be noted in the method for determination of carbon-sulphur compounds in gases by reduction in presence of platinised pumice to hydrogen sulphide, this latter being subsequently determined by any suitable method. The reduction takes place in contact with the finely divided metal at temperatures as low as 300°-350°. According to Lunge, however,[3] the method gives results of but moderate accuracy, since, if oxygen be present, oxidation of the hydrogen sulphide to sulphur occurs, with consequent low results. The method is, however, rapid and convenient, which cannot be claimed for the usual "referee test" for total sulphur, in which a measured quantity of gas is burned in a small burner, the sulphuric acid in the products being absorbed and estimated.

By comparison with the discussion on the removal of combined sulphur on the technical scale, given in Chapter VII., it will be seen that the catalytic decomposition of carbon-sulphur compounds is not confined to the platinum metals, but that nickel and iron, oxide of iron, pumice, and fireclay all assist the reduction process; at, however, more elevated temperatures for quantitative results.

Vogel[4] recommended a catalytic process for the qualitative detection of combined sulphur in illuminating gas. The test consisted in passing the gas through a heated tube containing strips of copper to retain the sulphur, which, on dissolving in nitric acid, gave a solution containing all the sulphur in the form of sulphate.

The method of Knorre and Arendt[5] for the determination of nitric oxide by reduction with hydrogen in a heated platinum capillary tube is another applied catalytic process. By slow passage through the heated tube, the reaction occurring is given by the equation

$$2NO + 2H_2 = 2H_2O + N_2.$$

There is a possibility of error, however, in that the reaction, if conducted too quickly, may proceed to the production of some ammonia, with consequent variation of the volume relationships upon which the method of estimation is based.

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[1] *Analyst*, 1919, **44**, 89.

[2] G. B. and H. S. Taylor, *J. Ind. Eng. Chem.*, 1922, **14**, 1008.

[3] *Technical Gas Analysis*, 1914, p. 256.

[4] *Ber.*, 1869, **2**, 741.

[5] *Ibid.*, 1899, **32**, 2136; 1900, **33**, 32.

In a similar manner nitrous oxide may be estimated, the reaction occurring being

$$N_2O + H_2 = H_2O + N_2$$

Owing to the difference in the two volume changes, this method can be applied to a mixture of both nitrous and nitric oxides

According to Treadwell,[1] Pollak has shown that carbon monoxide may be used as the reducing agent for nitric oxide provided the carbon dioxide be absorbed as it is formed

Dissociation processes.—The catalytic dissociation of nitrous oxide into its component elements has been recommended by Winkler,[2] cited by Woker[3] The gas, when passed through a heated platinum capillary, is converted into nitrogen and oxygen

$$2N_2O = 2N_2 + O_2,$$

and, from the increase in volume, the quantity of nitrous oxide may be determined Obviously, however, if hydrogen be present, the previously discussed reduction will occur

As is well known, most metals, even at the ordinary temperature, accelerate the decomposition of ozone, or are converted by it to peroxides Thus, the action is marked in the case of mercury, which, after treatment therewith, adheres in thin films to a glass containing vessel The conversion of bright metallic silver to a black superoxide is employed as a method of detection of the gas Lead, copper, nickel, and cobalt are similarly attacked, as well as many of the lower oxides, which are converted to peroxides, as, for example, lead and manganous oxides Manchot[4] has studied, in connection with the action of silver, the catalytic acceleration of the process by the presence of iron, and has shown that the minutest traces of this metal, preferably in the form of oxide, facilitate both the formation of the black peroxide and also the subsequent decomposition of the remaining ozone by means of the peroxide. The blackening is obvious, even in solutions containing but one part of ozone in 10,000 parts of the solution, and, with its aid, the presence of ozone in the hotter parts of gas flames is readily demonstrable

Ozone in presence of finely divided platinum is completely decomposed, yielding oxygen With this fact in view, Tommasi[5] suggested the determination of ozone in presence of chlorine and nitrous acid by the difference in titration of two standard ferrocyanide solutions when treated with samples of gas, with and without the previous decomposition process with platinum sponge

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[1] Vol ii p 567

[2] *Anleit z chem Untersuch d Industriegase*, 1893, p. 427

[3] *Katalyse in d anal Chem*, 1915, p 347

[4] *Ber*, 1906, **39**, 3510, 1907, **40**, 2891, 1908, **42**, 3948

[5] *Chem News*, 1879, **39**, 284.

A case of preferential decomposition studied by Richter[1] illustrates the analytical application of catalysis by nickel. It was shown that in a mixture of ethane, methane, and hydrogen the action of a heated nickel spiral brought about the decomposition of ethane to carbon and hydrogen. The methane, however, is slightly attacked if the reaction be carried to completeness. The tendency of ethane to decomposition into the elements is illustrated by Bone's experiment,[2] in which an explosion of a mixture of ethane and insufficient oxygen yielded a dense cloud of carbon. Mixtures of ethylene, hydrogen, and oxygen, and of acetylene, hydrogen, and oxygen with the same total carbon : hydrogen : oxygen ratio as in the ethane experiments, yielded practically completely carbon monoxide and hydrogen with little or no steam formation—another example of preferential combustion similar to those previously discussed.

Absorption processes.—In the absorption processes of gas analysis, by far the most important case of catalysis is one of inhibition, the retarding action of gases on the absorption of oxygen by phosphorus. In the analysis of coal gas, it is well known that the use of the phosphorus absorption pipette is not advisable, since traces of unsaturated hydrocarbons paralyse the activity of the phosphorus. Lunge[3] states that among the substances interfering with the absorption of oxygen are, according to Davy, Graham, and Vogel, hydrogen sulphide and phosphide, carbon disulphide, sulphur dioxide, iodine, bromine, chlorine, nitrogen peroxide, ethylene, acetylene, ether, alcohol, petroleum, oil of turpentine, cupione, creosote, benzene, ammonia, alcohol, tar, and many essential oils. Ethylene in concentration of 0·25 per cent by volume, it is further stated, is sufficient to produce the effect. Haber[4] found 0·17 per cent sufficient, while Hempel is of opinion that 0·04 per cent is sufficient. A considerable controversy has revolved around the supposed retarding action of methane and the higher saturated hydrocarbons. The experiments of Brunck, however, would seem to oppose the view that these act as negative catalysts, since it is stated that the disturbing substances can, in most cases, be removed by previous treatment of the gas with fuming sulphuric acid.

The mechanism of the retarding action is quite unexplained. Centnerszwer[5] associates the action with the unsaturated character of the inhibitors. Bancroft,[6] in a general discussion of catalyst poisons, shows that it is possible to "account for all the cases that have been considered if we postulate suitable and not improbable adsorptions", the poison being preferentially adsorbed and decreasing the normal adsorption in absence of the poison. The case of phosphorus, however, is not included in Bancroft's survey.

An error in the oxygen estimation by phosphorus absorption may be attributed to catalytic influence It is found, according to Baumann[1] and Leeds,[2] that carbon monoxide is oxidised by oxygen to carbon dioxide in presence of phosphorus This was denied by Remsen and Keiser,[3] but reiterated later by Baumann[4] and by Boussingault,[5] who, however, showed that the amount was exceedingly small, and has been attributed to the ozonising action of phosphorus on oxygen

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[1] Diss., Dresden, 1909.

[2] *Proc. Roy. Inst.*, 1908, **19**, 82.

[3] *Technical Gas Analysis*, 1914, p. 121.

[4] *Habilitationsarbeit*, Munich, 1896, p. 97.

[5] *Zeitsch. physikal. Chem.*, 1898, **26**, 21.

[6] *J. Physical Chem.*, 1917, **21**, 734.

Of catalytic accelerators in absorption processes, mention may first be made of the addition of alkali to pyrogallol in order to promote the rate of absorption of oxygen Originally discovered by Dobereiner, it was introduced into gas analysis by Liebig, and provides an absorption agent of high efficiency The addition of mercury sublimate to alkaline solutions of pyrogallol in order to accelerate the absorption of oxygen has also been proposed[6] Its use, however, increases the possibility of carbon monoxide formation from the pyrogallol, which has been shown by a number of investigators[7] to hinder exact work, unless the carbon monoxide can be removed prior to the taking of the volume reading

The addition of vanadic oxide or of uranyl sulphate to strong sulphuric acid (sp gr 1 84) is recommended by Lebeau and Damiens[8] as a rapid absorption agent for olefines in place of fuming sulphuric acid Lommel and Engelhardt[9] have recently claimed that silver sulphate is an excellent accelerator of reaction between ethylene and sulphuric acid. They state that addition of ethylene to the silver salt occurs as a first stage in the process They suggest that the ethylene tension is so diminished that the method may be used for analytical purposes, if phosphoric acid is added to the silver salt solution A trial of their proposed solution did not, however, give one of the authors (H S T) as satisfactory results as the bromine method

CATALYSIS IN INORGANIC ANALYSIS

Oxidation processes.—Of considerable importance in analytical technique, and at the same time of great interest from the theoretical point of view, is a series of volumetric operations in which potassium permanganate is employed as oxidising agent The catalytic influence of manganese sulphate in all these reactions has long been known and studied Thus Harcourt and Esson[10] observed the accelerating action of manganese sulphate formed during the reaction between potassium permanganate and oxalic acid, when conducted in presence of sulphuric acid. A study of the kinetics of the process was made, in which it was shown that, for a given time interval, the velocity of reaction, in presence of a constant quantity of permanganate but with varying amounts of oxalic acid, sulphuric acid, and manganese sulphate, was proportional to the amounts of sulphuric acid and manganese sulphate initially present, and also dependent on the quantity of oxalic acid, but in no simple proportionality. It was shown that, with oxalic acid in excess, permanganate disappeared with time in accordance with the unimolecular law.

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[1] *Ber*, 1883, **16**, 1146

[2] *Chem. News*, 1883, **48**, 25

[3] *Amer Chem J*, 1883, **4**, 454

[4] *Ber*, 1884, **17**, 283

[5] *Compt rend*, 1864, **58**, 777

[6] Stassana, *Compt rend Soc de Biol*, 1905, **58**, 96

[7] See Clowes, *Zeitsch anal Chem*, 1897, **36**, 504

[8] *Compt rend*, 1913, **156**, 557.

[9] *Ber*, 1924, **57**, 848, B P 185787

[10] *Phil Trans*, 1866, **156**, 201

At a much later period Schilow reinvestigated the reaction kinetics.[1] He showed that, with the oxalic acid in great excess, the progress of the reaction can be expressed by the velocity equation

$$\frac{dx}{dt} = k(a - x)x,$$

where a denotes the original permanganate concentration, and x the amount converted into manganese sulphate in the time t. With initial concentration, b, of manganese sulphate, the reaction equation would therefore be

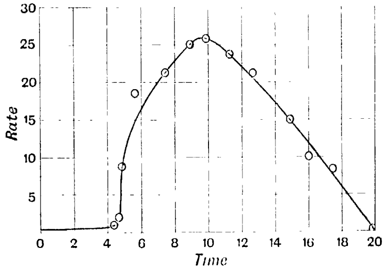

FIG. 26.

$$\frac{dx}{dt} = k(b + x)(a - x).$$

It can be readily demonstrated mathematically in regard to the former of these two equations that the maximum velocity is attained when

$$x = \frac{a}{2},$$

and in the second case the same is true when

$$x = \frac{a - b}{2}.$$

This conclusion was experimentally verified in both cases, it being shown that, starting slowly, the rate of reaction steadily increased, until, at the period of half-decomposition, it attained its maximum and then fell away. The plot of an experimental curve in an experiment in initial absence of manganese sulphate is given in Fig. 26. The reaction forms, therefore, a beautiful example of induction, in which it must be observed that the phenomenon is due to the autoproduction of catalytic agents, and not, as in the hydrogen-chlorine combination, to the progressive displacement of retarding agents

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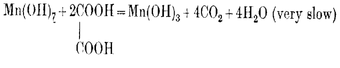
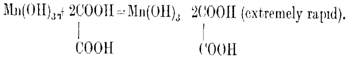
[1] *Ber.*, 1903, **36**, 2735.

Schilow concluded from these studies that the concentration of oxalate, so long as it was in excess, practically did not influence the reaction, and that what was being measured was the velocity of the reaction between the higher and lower states of oxidation of manganese. The equations representing this view would be

(1) 

$$Mn(OH)_7 + 2\underset{\displaystyle COOH}{\overset{|}{COOH}} = Mn(OH)_3 + 4CO_2 + 4H_2O \text{ (very slow)}$$

(2) 

$$Mn(OH)_3 + 2\underset{\displaystyle COOH}{\overset{|}{COOH}} = Mn(OH)_3 \; 2\underset{\displaystyle COOH}{\overset{|}{COOH}} \text{ (extremely rapid).}$$

(3) $Mn(OH)_7 + Mn(OH)_3 \; 2(COOH)_2$

$$= 2Mn(OH)_3 + 4CO_2 + 4H_2O \text{ (measured)}$$

The last reaction apparently, according to Schilow, may represent the sum of two successive reactions

(3*a*) $Mn(OH)_7 + Mn(OH)_3 \; 2(COOH)_2$

$$= Mn(OH)_6 + Mn(OH)_4 \; 2(COOH)_2 \text{ (measured).}$$

(3*b*) $Mn(OH)_4 \; 2(COOH)_2 + Mn(OH)_6$

$$= 2Mn(OH)_3 + 4CO_2 + 4H_2O \text{ (extremely rapid).}$$

It is, however, to be understood, according to Schilow, that the above scheme of reaction applies only to the particular conditions chosen by him Alterations in the acid concentrations employed, raising the temperature above 25°, and the addition of catalysts such as iron, chromium, and silver salts, would all tend to increase the velocity of the first reaction, and lead, therefore, to a different velocity equation of the form

$$\frac{dx}{dt} = k_1(a-x)^n(c-x)^m + k_3x(a-x),$$

c in this equation referring to the concentration of oxalate, k_1 and k_3 to the constants of the equations (1) and (3)

Schilow extended these studies[1] in his researches on the coupling of chemical reactions, and concludes that the above conclusions are applicable generally to permanganate oxidation of such oxy-acids, *e g* tartaric acid, as show a tendency towards complex formation

A somewhat different conclusion is reached by Skrabal[2] He assumes, like Schilow, an intermediate stage of oxidation and an intermediate product, the manganic ion, which reacts with oxalic acid more rapidly than the permanganic ion. He distinguishes three periods in the reaction: (1) The incubation period, in which permanganate and oxalic acid interact to give carbon dioxide and manganic ion, which latter reacts extremely rapidly with further oxalic acid to give the manganous salt and more carbon dioxide. The reactions would be

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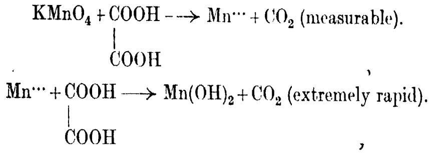
[1] *Zeitsch physikal Chem*, 1903, **42**, 661

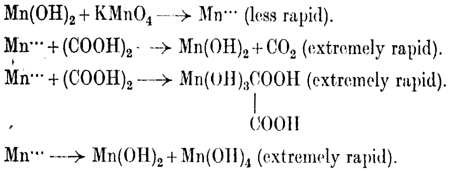
[2] *Zeitsch anal Chem*, 1903, **42**, 329, *Zeitsch anorg Chem*, 1904, **42**, 60, *Zeitsch. Elektrochem*, 1905, **11**, 653



$$\mathrm{KMnO_4} + \begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} \dashrightarrow \mathrm{Mn^{\cdots}} + \mathrm{CO_2} \text{ (measurable).}$$

$$\mathrm{Mn^{\cdots}} + \begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} \longrightarrow \mathrm{Mn(OH)_2} + \mathrm{CO_2} \text{ (extremely rapid).}$$

(2) The period of induction, in which the manganous oxide and permanganate interact to yield the manganic ion, which reacts, as above, but which tends also to form an oxalate complex and the oxidation stages Mn^{II} and Mn^{IV}, according to the scheme:



$$\mathrm{Mn(OH)_2} + \mathrm{KMnO_4} \longrightarrow \mathrm{Mn^{\cdots}} \text{ (less rapid).}$$

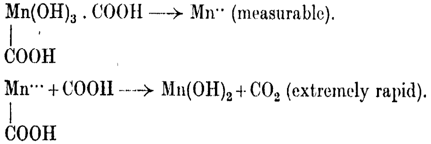
$$\mathrm{Mn^{\cdots}} + \mathrm{(COOH)_2} \longrightarrow \mathrm{Mn(OH)_2} + \mathrm{CO_2} \text{ (extremely rapid).}$$

$$\mathrm{Mn^{\cdots}} + \mathrm{(COOH)_2} \longrightarrow \mathrm{Mn(OH)_3}\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} \text{ (extremely rapid).}$$

$$\mathrm{Mn^{\cdots}} \longrightarrow \mathrm{Mn(OH)_2} + \mathrm{Mn(OH)_4} \text{ (extremely rapid).}$$

(3) The end period, which is twofold in nature, corresponding with the disappearance of the manganic-oxalate complex and of the conversion of Mn^{II} and Mn^{IV} to manganous oxide, the retardation in the end period being attributed to the slow decomposition of the manganic-oxalate complex:

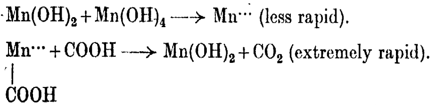
End period (*a*).



$$\begin{array}{l}\mathrm{Mn(OH)_3 \,.\, COOH}\\ \quad\quad\quad\quad\;\, |\\ \quad\quad\quad\;\; \mathrm{COOH}\end{array} \longrightarrow \mathrm{Mn^{\cdot\cdot}} \text{ (measurable).}$$

$$\mathrm{Mn^{\cdots}} + \begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} \longrightarrow \mathrm{Mn(OH)_2} + \mathrm{CO_2} \text{ (extremely rapid).}$$

End period (*b*).



$$\mathrm{Mn(OH)_2} + \mathrm{Mn(OH)_4} \longrightarrow \mathrm{Mn^{\cdots}} \text{ (less rapid).}$$

$$\mathrm{Mn^{\cdots}} + \begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} \longrightarrow \mathrm{Mn(OH)_2} + \mathrm{CO_2} \text{ (extremely rapid).}$$

The permanganate titration of iron in presence of hydrochloric acid.—Lowenthal and Lennsen[1] showed that in titrating ferrous iron with permanganate solution, more permanganate was required than theory demands if the iron solution was acidified with hydrochloric acid, and that this could be explained as being due to an induced reaction of the type studied by Kessler[2] Interaction occurred between the hydrochloric and permanganate with production of chlorine, thus using permanganate in excess of that required by the iron This reaction, which ordinarily would not occur, is induced by the simultaneous oxidation of the ferrous salt, the reaction being representable by the equation

$$16HCl + 2KMnO_4 = 2KCl + 2MnCl_2 + 5Cl_2 + 2H_2O$$

Kessler showed[3] that the addition of manganous salts prevented chlorine evolution The reaction was carefully studied by Skrabal,[4] who associated the chlorine production, as had Zimmermann previously,[5] with the formation by the permanganate of a higher oxide of iron, which, according to Manchot,[6] was to be regarded as Fe_2O_5 The two reactions occurring would therefore be (*a*), the main reaction,

$$Fe_2O_5 + 4Fe = 3Fe_2O_3,$$

and (*b*), the induced reaction,

$$Fe_2O_5 + 4HCl = Fe_2O_3 + 2H_2O + 2Cl_2$$

Within limits, it was shown that, with rising ferrous ion concentration and decreasing hydrochloric acid concentration, the excess permanganate required was decreased

The addition of manganous sulphate, it was shown, corrected the tendency to chlorine production, not by a retarding influence on the induced reaction, but by its strongly catalytic effect on the iron oxidation process, giving it a velocity so great that negligible quantities only of hydrochloric acid have the time to oxidise Skrabal showed that the theoretical aspects of the oxidation process gave results as to mode of operation which were in substantial agreement with those actually found in analytical practice

Treadwell gives data of Zimmermann and Reinhardt for permanganate titration of vanadium in presence and absence of iron Muller and Diefenthaler[7] carry out the process in hydrochloric acid solution with addition of manganous salts, which accelerate the primary reaction as in the case of iron just considered The corresponding reactions with tungsten and molybdenum were investigated by van der Pfordten.[1] Follenius[2] showed that with uranium salts the same induced reaction occurs, and Zimmermann[3] showed the importance of addition of the manganous salts in the titration process. In the well-known Volhard method for permanganate determination of manganese,[4] which subsequently has been modified by a considerable number of analysts, manganese sulphate acts similarly as an accelerator the reaction occurring according to the general equation

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[1] *Zeitsch anal Chem* , 1861, **1**, 329 , *J pr Chem* , 1862, **86**, 193

[2] *Pogg Ann* , 1855-63, **95**, **96**, **113**, **118**; **119**

[3] *Ibid* , 1863, **118** 48 , **119**, 225

[4] *Zeitsch anal Chem* , 1903, **42**, 359 , *Zeitsch anorg Chem* , 1904, **42**, 48, 76

[5] *Ber* , 1881, **14**, 779 , *Zeitsch anal Chem* , 1882, **21**, 307

[6] *Annalen*, 1902, **325**, 93

[7] *Zeitsch anorg Chem* , 1911, **71**, **343.**

$$2MnO_4' + 3Mn^{\cdot\cdot} + 2H_2O \rightarrow 5MnO_2 + 4H^{\cdot}.$$

In the previously cited research of Skrabal[5] a theoretical investigation is made of the low results which may be obtained. These latter are due to the incompleteness of the oxidation of the manganese to dioxide, owing to simultaneous precipitation of unoxidised manganous oxide with the dioxide. According to Skrabal this precipitation tends to occur owing to the decomposition of the manganic oxide formed in the first stages of oxidation :

$$4Mn^{\cdot\cdot} + MnO_4' + 8H' = 5Mn^{\cdot\cdot\cdot} + 4H_2O.$$

The trivalent manganese then decomposes according to equation :

$$2Mn^{\cdot\cdot\cdot} \rightarrow Mn^{\cdot\cdot\cdot\cdot} + Mn^{\cdot\cdot}.$$

The analytical methods employed have, as their aim, the suppression of the precipitation of the manganous oxide, which reacts with further quantities of permanganate until completely converted into the dioxide.

Finally, the same catalytic phenomenon is to be observed in the titration of hydrogen peroxide solutions with permanganate, and in the titration of sulphites. In the latter case Honig and Zatsek[6] express the opinion that low results are due to formation of a certain amount of dithionate, which Milbauer[7] proposes to suppress by working with excess of permanganate, strongly acidified with sulphuric acid, to which the sulphite solution is added, the excess permanganate being titrated by oxalic acid solution.

Ferrous sulphate may be employed as accelerator in the qualitative test for hydrogen peroxide. The liberation of iodine from potassium iodide solutions by hydrogen peroxide is ordinarily an extremely slow process ; by addition of ferrous sulphate the reaction proceeds rapidly, and is also extremely sensitive, so that minute traces of the peroxide may be detected.[8] The peroxide-iodide reaction is inhibited by acids, and does not occur, even in presence of ferrous sulphate, in acid solutions. If, however, a ferrous-copper sulphate mixture is employed, the sensitivity of the test is restored, a remarkable case of activation.

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[1] *Ann. Chim.*, 1884, **222**, 137 ; *Zeitsch. anal. Chem.*, 1884, **23**, 413.

[2] *Zeitsch. anal. Chem.*, 1872, **11**, 179.

[3] *Ann. Chim.*, 1882, **213**, 285.

[4] *Ibid,*, 1879, **198**, 318.

[5] *Zeitsch. anorg. Chem.*, 1904, **42**, 60.

[6] *Monatsh.*, 1887, **4**, 738.

[7] *Zeitsch. anal. Chem.*, 1909, **48**, 17.

[8] Schönbein, *J. pr. Chem.*, 1850, **79**, 66.

Price[1] noted the catalytic activity of ferrous sulphate in the interaction of potassium persulphate and potassium iodide:

$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2,$$

showing that the normal bimolecular reaction was accelerated proportionately to the concentration of the catalyst, yielding, therefore, a velocity equation of the form

$$\frac{dx}{dt} = kc(a - x)(b - x),$$

where c denoted the concentration of catalyst, and a and b the initial concentrations of the reactants The reaction occurring may be applied to the analytical determination of the persulphate

Of further oxidation processes in analytical chemistry in which catalytic activity is invoked, mention may be made of the influence of alkalis in promoting oxidation processes Thus the oxidation of the arsenious to the arsenic stage by chlorine and bromine takes place rapidly in alkaline solutions

Reduction processes.—In the operation of reduction processes in chemical analysis with the hydrogen evolved by interaction of metals and acids or alkalis, the catalytic rôle is well illustrated

As is well known, nitrates, nitrites, and chlorates may all be determined analytically by reduction, in the first two cases to ammonia, in the last to chloride, followed by subsequent estimation of the reduced product Further, the reduction of solutions containing iron salts, prior to estimation by permanganate, is also an analytical operation of frequent and important use To effect the reduction, numerous methods of generating the hydrogen have been adopted, both in acid and in alkaline solutions

For the reduction of nitrates in acid solutions zinc was originally employed as reducing agent, but, owing to the tendency which is exhibited by this metal to yield the easily decomposed nitrous acid and the consequent errors due to loss of nitrogen, zinc has been abandoned in favour of iron Ulsch[2] showed that reduction of nitrates, using iron and sulphuric acid, yielded ammonia quantitatively without the formation of the intermediate products It was found also that the ferrous sulphate produced in the course of the reaction:

$$2KNO_3 + 8Fe + 10H_2SO_4 = K_2SO_4 + 8FeSO_4 + (NH_4)_2SO_4 + 6H_2O,$$

accelerated the reducing action in marked degree

In addition, however, to the catalytic influence of the reaction products, the reduction phase may also be modified by the use of activated metals as agents for hydrogen production. In the case of zinc, it was shown by Williams[3] that in the determination of nitrates in water the substitution of a zinc-copper couple, as orginally employed by Gladstone and Tribe, for the ordinary zinc dust gave a reagent extraordinarily well suited to the purposes of reduction, and capable of further acceleration by addition of neutral salts and dilute acids. Ulsch[1] showed that the corresponding copper-iron couple was a more active agent than iron alone, and in suitable circumstances could be operated at the ordinary temperature. The use of such an agent also possesses the advantage that the ferrous sulphate formed neutralises the inhibitory effects which chlorides exert in the reduction of the nitrates. Schmidt[2] employed a zinc-iron mixture in acid solutions.

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[1] *Zeitsch physikal Chem*, 1898, 27, 474

[2] *Zeitsch anal Chem*, 1891, 30 175

[3] *Analyst*, 1881, 6, 36.

In a similar manner the use of the zinc-copper couple as agent for the reduction of chlorates to chlorides has been studied and recommended by Thorpe and Eccles[3] and by Bothamley and Thompson.[4]

The reduction of solutions of ferric salts by zinc amalgam in sulphuric acid solution is another application of the activated metal in analytical chemistry. Müller and Wegelin[5] show that the reducing agent is eight to nine times more completely used in the case of the amalgam than with pure zinc, although the reaction velocity is slower. By addition of copper sulphate solutions in minimal amounts, the reaction velocity of the amalgam may be so far accelerated as to overcome this disadvantage. Copper and silver in the metallic state, according to Müller and Wegelin, also catalyse the reduction of iron by zinc amalgam, presumably by interaction of the metal with ferric iron:

$$\mathrm{Cu} + \mathrm{Fe}^{\cdot\cdot\cdot} = \mathrm{Fe}^{\cdot\cdot} + \mathrm{Cu}^{\cdot},$$

and subsequent reduction to the metallic state of the zinc.

In the alkaline reduction of nitrates it was shown by Vernon Harcourt[6] that, using zinc and aqueous potash as reducing agent, only three-quarters of the nitrate was converted into ammonia. On the other hand, if a mixture of zinc and iron was employed, reduction was complete. In place of the zinc-iron mixture, zinc slightly covered with a coating of copper has also been employed.

Reduction in alkaline solution with aluminium results in complete conversion of nitrates to ammonia. Modern developments of the alkaline method, however, mainly employ a ternary alloy of aluminium, copper, and zinc, known as Devarda's alloy, after the inventor.[7] The original alloy was composed of 50 parts of copper, 45 parts of aluminium, and 5 parts of zinc. Later specifications suggest 39 parts of copper, 59 parts of aluminium, and 2 parts of zinc. The attack by alkali is very rapid and energetic, and, after a half-hour's reduction, distillation of the ammonia may be undertaken with quantitative results.

The use of sodium amalgam for reduction of nitrates is yet another application of the principle of activation.

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[1] *Loc. cit.*

[2] *Chem. Zeit.*, 1893, **17**, 173.

[3] *J. Chem. Soc.*, 1873, **26**, 541.

[4] *Ibid.*, 1888, **53**, 164.

[5] *Zeitsch. anal. Chem.*, 1911, **50**, 615.

[6] *J. Chem. Soc.*, 1862, **15**, 385; 1863, **16**, 289.

[7] *Chem. Zeit.*, 1892, **16**, 1952.

The theoretical explanation of the principle of activation is to be sought largely in the electro-chemical behaviour of such alloys as compared with the single metals As such, the matter has been fully treated elsewhere (Chapter XV p 424), and so it is not necessary here again to enlarge upon the point A further factor of possible influence has been emphasised by Bodlander,[1] who associates catalytic activity in such cases with the rate and state of evolution of hydrogen from such metallic couples It is at the metal surfaces that the reduction undoubtedly occurs, and the nature and composition of such surfaces may determine the nature of the hydrogen evolution and the participation of the gas in the reducing action

CATALYSIS IN ORGANIC ANALYSIS

Elementary analysis. Historically considered, the most important application of catalysis in organic analysis is to be found in the determination of the composition of organic compounds by methods of combustion The familiar method of determining carbon and hydrogen in such materials by combustion with oxygen in presence of copper oxide is at once a classical example of catalysis and an operation of fundamental import to the organic chemist Gay-Lussac in 1816 employed copper oxide in the analysis of uric acid and the process was immediately tested and found applicable by Dobereiner, Prout, and Beraud[2] In all these cases, however, the material to be analysed was mixed intimately with the copper oxide and thus brought to combustion The modern developments of the process date from the time of Liebig, whose investigations of the operation determined the lines of subsequent procedure, converting the process to one of combustion of the organic compound with oxygen in presence of the copper oxide as catalyst

Modifications of the copper oxide method have been largely developed during the past two decades, more especially in the direction of substituting for copper oxide, platinum, in suitable form, as contact agent The adoption in many present-day laboratories of the simplified method of analysis due to Dennstedt is evidence for the progress which such modifications have made

The high activity of suitably prepared platinum in the oxidation of the products of organic combustion was demonstrated by Kopfer[3] He employed a mixture of platinum black and asbestos in order to obtain a maximum surface effect for the contact material, and with substances containing carbon, hydrogen, and oxygen only, a combustion tube containing the substance in a boat followed by the platinum asbestos is all that is required besides the usual absorption agents for carbon dioxide and water. With nitrogen-, sulphur-, and halogen-containing bodies the usual absorption agents for such substances were required.

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[1] *Fifth Int Cong App Chem*, 1903 p 635

[2] *Schweigger's J*, 1816, **16**, **17**, 1818, **22**, 1820, **29**

[3] *Zeitsch anal Chem*, 1878, **17**

Claesson[1] utilised heated platinum in a method for determining sulphur in organic compounds. The substance was burnt in an atmosphere of oxygen containing oxides of nitrogen, which, on subsequent contact with heated platinum, oxidised the sulphur to sulphuric acid, which could then be absorbed in water and estimated. Claesson extended the process to the determination of halogens, and this was likewise proposed by Schwarz[2] for the determination of bromine, and by Zulkowsky and Lepéz[3] for halogens generally. These latter suggested platinised quartz as contact material, the absorption agent being ammoniacal hydrogen peroxide, which absorbed all the halogen acid produced in the process and reduced any free halogen formed to the corresponding acid, according to the equation

$$H_2O_2 + X_2 = 2HX + O_2.$$

Various experimental modifications of the use of platinum were made from time to time. Thus the use of platinum combustion tubes was recommended,[4] without, however, any considerable development. Electrical heating of platinum spirals has frequently been recommended.[5] The elaboration of the method of organic analysis, employing platinum as contact material, is due, however, mainly to the researches of Dennstedt, who has succeeded in perfecting a method of analysis of organic compounds, whereby, in one operation, carbon, hydrogen, nitrogen, sulphur, and halogen may all be estimated.

The essential principles upon which the Dennstedt method of analysis is based may be here outlined, the actual experimental details being, however, eliminated, since these are readily obtainable in the modern texts of practical organic chemistry as well as in the original literature.[6] The contact material originally employed was composed of platinum (obtained by ignition of the pyridine double salt) or of platinised quartz. Later, use was made of thin pieces of platinum foil, star-shaped and fitted on to a central strip of foil 6-8 cm. long. The advantage of using foil over the finely divided preparations lies in the fact that minimal amounts only of sulphuric acid are retained by the foil, whereas using platinised asbestos marked amounts of the acid may be occluded, most probably by the asbestos as well as the platinum. In the earlier forms of apparatus, some few centimetres beyond the contact mass, in the combustion tube, were placed two weighed boats containing finely divided silver, which, in the operation of the process, were heated to *circa* 300° and served to retain halogens and the sulphur, which, in the course of the oxidation process, had been converted to sulphuric acid Beyond these boats were placed two weighed porcelain boats filled with lead superoxide to absorb any sulphurous acid and nitrogen dioxide As was first shown by Henry,[1] lead superoxide may be used as absorption agent in sulphur determinations, and Warren[2] utilised this absorption for quantitative determinations Kopfer employed the same material for retaining oxides of nitrogen. The operating temperature for the lead peroxide is *circa* 150° Calcium chloride and potash or soda-lime absorption apparatus are attached to the combustion tube for determination of water and carbon dioxide The addition of a bubbler containing palladium chloride solution to the end of the apparatus serves as an indicator that combustion is complete, since incomplete oxidation causes a blackening of the solution, due to reduction

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[1] *Zeitsch. anal. Chem.*, 1883, **22**, 177 ; *Ber.*, 1886, **19**, 1910 . 1887, **20**, 3065.

[2] *Monatsh.*, 1882, **3**, 726.

[3] *Ibid.*, 1884, **5**, 537.

[4] Gooch, *Amer. Chem J.*, 1880-88, **2**, 247 ; Dudley, *ibid* , 1888, **10**, 433.

[5] Carrasco and Planchen, *Gazzetta*, 1906, **36**, 492 ; Breleau and Leroux, *Compt rend.*, **1907, 145**, 524 ; Milschsack and Roth, *Zeitsch. angew. Chem* , 1914, **27**, 5.

[6] See, for example, Dennstedt, *Die Entwicklung der organischen Elementaranalyse* ; *Ahrens Sammlung*, Bd. **4**, Stuttgart, 1899 ; *Anleitung zur vereinfachten Elementaranalyse*, Hamburg, 1906 ; *Zeitsch. angew. Chem.*, 1897, **10**, 462 ; 1904, **17**, 30 ; 1905, **18**, 320, 1134, 1562 ; *Zeitsch. anal. Chem.*, 1901, **40**, 612 ; 1902, **41**, 525 ; 1903, **42**, 417 ; 1906, **45**, 26 ; 1907, **46**, 26 ; *Ber.*, 1897, **30**, 1592 ; 1905, **38**, 3730 ; 1906, **39**, 1623 ; 1907, **40**, 3677, 4300 ; 1908, **41**, 600, 2778.

If, in addition to carbon, hydrogen, and oxygen, halogens alone are present, the increase in weight of the vessels containing silver gives the amount of halogen present If nitrogen be present but not sulphur, the increase in weight of the lead peroxide corresponds with the amount of nitrogen present Sulphur, when present, is divided between the vessels containing silver and the lead peroxide, and when associated in the original material with halogen and nitrogen must be separated therefrom in the two cases This is effected thus the sulphur is present in the vessels containing silver as the sulphate and is separated from the halides by digestion of the silver with water, whereby the sulphate is dissolved, and may then be added to the sulphate in the superoxide The halogens are then extracted from the silver by means of potassium cyanide and determined in the usual gravimetric manner after elimination of the cyanide by boiling with nitric acid For the determination of sulphur and nitrogen in the lead peroxide, the residue after combustion is extracted with 33 per cent alcohol in which the sulphate is precipitated The alcoholic extract is made up to 100 c c. and an aliquot portion thereof evaporated to give the quantity of nitrate present

In later modifications of the Dennstedt process it has been found advantageous to eliminate the silver vessels in all cases except those in which iodine is to be estimated Bromine and chlorine are absorbed quite conveniently by lead peroxide, iodine, however, is not retained. In substances containing nitrogen, sulphur, chlorine, and bromine, the lead peroxide is extracted with sodium carbonate or bicarbonate solution (3-4 per cent) in the cold for twenty-four hours, or for several hours in a shaking machine The filtrate is then divided into aliquot portions, which are then separately analysed for sulphur, by precipitation as sulphate, and for halogens, by precipitation as the silver halide; the nitrogen, if present, being obtainable by difference.

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[1] *J. Pharm Chim.*, 1849, 20, 59

[2] *Zeitsch anal Chem.*, 1866, 5, 169.

Halogen estimations in organic compounds.—An elegant application of catalytic hydrogenation to the determination of halogens in organic compounds is of quite recent date. It was shown by Borsche and Heimburger[1] that organic halogen compounds when heated with hydrogen in presence of the colloidal platinum metals were converted to the hydrogenated products with simultaneous liberation of the halogen acid. This reaction was applied by Busch and Stove[2] to the analytical estimation of halogens in such compounds, using palladium deposited on calcium carbonate as the catalytic agent. The liberated acid was neutralised as formed by alkali present in the aqueous or alcoholic solution of the compound. Solvents such as benzene and acetone were found to inhibit the catalytic activity of the metal. The halogen, after liberation from the organic material, was estimated by simple titration. It was claimed that by the use of calcium carbonate as support material for the catalytic agent recovery of the metal was facilitated, thus minimising expense. Subsequent researches, however, of C. Kelber[3] showed that nickel could be used as an excellent substitute for platinum and palladium colloids as catalytic agent, thereby eliminating the factor of expense in the analytical method. It was shown that with a suitable shaking arrangement to ensure intimacy of contact between the hydrogen and the nickel suspension, the conversion to the hydrogenated product was rapid. Numerous examples were quoted, both in the papers of Busch and Stove and of Kelber, to show the accuracy of the process, and this is confirmed by a further report of Rosenmund and Zetsche[4] on numerous halogenated bodies investigated prior to 1914.

The Kjeldahl process for estimating nitrogen.—This process for estimating nitrogen in organic compounds by conversion of the nitrogen content into ammonium sulphate by digestion of the compound with concentrated sulphuric acid is normally operated with the assistance of a catalytic agent. As operated by Dyer,[5] the addition of a globule of mercury to the sulphuric acid is recommended. The mercuric sulphate thus produced acts as a promoter of the oxidation process, hastening the production of the clear, colourless liquid which must be obtained before estimation of the ammonia produced.

The Kjeldahl method is not applicable to a considerable number of organic compounds containing nitrogen, principally the nitro-derivatives and compounds having nitrogen in a ring system, as, for example, pyridine derivatives. In such cases effort has been made to render the process applicable by addition of such derivatives as the carbohydrates, sugars, and phenols, or by variation of the oxidising agent In the latter connection, potassium permanganate, manganese dioxide, copper sulphate, phosphoric anhydride, disodium phosphate, platinic chloride, and magnesia have all been suggested as catalytic agents

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[1] *Ber.*, 1915, **48**, 452, 850.

[2] *Ibid.*, 1916, **49**, 1063.

[3] *Ber.*, 1917, **50**, 305.

[4] *Ibid.*, 1918, **51**, 578.

[5] *J. Chem. Soc.*, 1895, **67**, 811.

The identification and estimation of organic compounds.—The analytical operations which are involved in determining the identity and composition of organic compounds are in very great measure the application of catalytic processes The primary operation in organic analysis is, naturally, the preparation of the substance under investigation in the highest possible degree of purity Following this operation there arises its assignment to a definite class of compound, and, at this stage of the problem, processes of resolution into simpler or more readily identified products largely arise Hydrolysis therefore plays a large part in such operations and the aid of catalytic agents is usual. Further, certain catalytic reactions are characteristic to definite classes of organic compounds and may be utilised in the process of identification, whilst in the determination of the individuality of a member of a given class catalytic reactions may also frequently be invoked By a reference to the main classes of organic compounds concerned, these generalised remarks may be illustrated

Alcohols.— Of catalytic operations in the identification of alcohols, esterification processes rank high in importance

Stephan[1] proposed the use of phthalic anhydride as a suitable acidic agent for the esterification process of identification and as a means of distinction between primary, secondary, and tertiary alcohols Stephan found that primary alcohols reacted quantitatively to form the acid ester on being heated with the anhydride for an hour in a suitable solvent such as benzene, whereas secondary alcohols react with difficulty and tertiary alcohols not at all under the given conditions Following the investigations of Menschutkin and others (Chapter XII), the velocity of esterification with a given alcohol under given conditions is applicable for purposes of identification

Hell's method[2] for identification of primary alcohols of high molecular weight is, in reality, the dehydrogenation of an alcohol with simultaneous production of an acid Soda-lime is the particular agent employed, though doubtless other catalytic agents could be used The reaction occurring may be represented by the equation

$$R\ CH_2\ OH + KOH = R\ COOK + 2H_2$$

In the process the possibility of further decomposition of the acid, according to the equation

$$R\ COOK + KOH = R\ H + K_2CO_3,$$

must be observed Especially with lower primary alcohols is this reaction predominant. According to Bancroft[1] the dehydrogenation process takes place in several stages, representable by the equation

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[1] *J pr Chem*, 1899 (ii.), **60**, 248

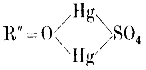
[2] *Ann. Chim*, 1884, **223**, 269.

$$\begin{aligned} CH_3.CH_2.OH + NaOH &= CH_3.CHO + NaOH + H_2O \\ &= CH_2.CO + NaOH + 2H_2 = CH_3.COONa + 2H_2. \end{aligned}$$

The caustic soda is the catalytic agent, the lime being practically inert at the temperatures of operation.

In the oxidation of alcohols the use of catalytic agents is possible, and the variation in the reaction products, aldehyde and acid from primary alcohols, ketones from secondary alcohols and ketones, and acids of lower carbon atom content from the tertiary alcohols, serves to indicate the type of alcohol under study.

The tendency of the tertiary alcohols to form ethylenic hydrocarbons permits of the application of the reaction of Denigès,[2] whereby, on heating a few drops of the alcohol with a solution of mercuric oxide in dilute sulphuric acid, a yellow or red precipitate of the characteristic compounds



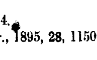
is obtained.

For the phenols, the coloration test with ferric chloride is the most general method of identification, and consequently catalytic operations are but little employed. It may be observed, however, that in acid esterification processes the phenols, in general, do not yield esters except in those cases in which, owing to substitution in the ring, the hydroxyl group is rendered strongly negative.

Acids.—As with alcohols, esterification is largely employed in the identification of organic acids, and the general methods of catalytic acceleration as outlined in a preceding chapter are applicable. The velocity of esterification may be utilised to differentiate between primary, secondary, and tertiary acids, in which case the data compiled by Menschutkin and others on constitution influences in esterification are employed. In general the esterification method of Fischer and Speier[3] is adopted for purposes of identification.

Anhydrides and lactones.—Processes of hydrolysis with subsequent identification of the acids produced are employed in the analysis of anhydrides and lactones. The earlier discussion of these reactions outlines the catalytic principles involved and the agencies employed for promotion of the reaction.

The carbonyl grouping.—In the identification of ketones, aldehydes, sugars, and other organic compounds containing the characteristic carbonyl grouping,



$$\begin{matrix} R \\ & \rangle C=O, \\ R_1 \end{matrix}$$

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[1] *J. Physical Chem.*, 1917, **21**, 594.

[2] *Compt. rend.*, 1898, **126**, 1277.

[3] *Ber.*, 1895, **28**, 1150, 3252.

the possibility of applying catalysis is most marked Fischer's method[1] of identification of the carbonyl grouping by conversion to the phenylhydrazine derivatives is markedly influenced by catalytic agents both positive and negative. Ordinarily, the reaction is carried out by warming the substance with phenylhydrazine hydrochloride in weak acetic acid solution, but Schottle[2] has directed attention to the inhibitory effect of small amounts of this acid as well as of the free mineral acids such as hydrochloric, sulphuric, and especially nitrous acid The reaction, however, occurs much more rapidly in pure acetic acid than in water, and in this solvent proceeds even at the ordinary temperature[3] The insolubility of the hydrazones in acetic acid may account for this observation In researches on the catalytic activity of zinc chloride, Reddellen[4] has observed the accelerating action of this compound, in the form of a phenylhydrazine complex $(C_6H_5 . NH\ NH_2)_2ZnCl_2$, on the Fischer reaction for ketones

The corresponding reaction of the carbonyl grouping with hydroxylamine,[5] whereby aldoximes and ketoximes are produced, is similarly retarded, according to Schottle,[6] by the presence of mineral acids Caustic potash and soda, on the other hand, act as accelerators[7]

The catalytic features of the aldol condensation as applied to the identification of aldehydes has been previously considered (p 405)

Oxidation and reduction of the carbonyl grouping with subsequent identification of the resulting products may also be employed in the determination of aldehydes and ketones, with simultaneous application of catalytic methods

The use of alkali in promoting the iodoform reaction for acetone is a specific example of catalysis in organo-analytical practice, applicable both qualitatively and quantitatively[8]

Carbohydrates and sugars.—The reaction of the sugars with phenylhydrazine to yield hydrazone and osazone is due to Fischer,[9] and was used by him in the identification and elucidation of the various possible isomers

Maquenne[10] proposed to utilise the yield of the reaction to yield osazone, under definite conditions of concentration, temperature, and time, as a method of identification of the various sugars Under the prescribed conditions it was found that the yield of hydrazone from 1 grm. of sugar was greatest in the case of sorbose and least with lactose and maltose

The Tollens reaction is principally employed in the identification of pentoses. This reaction is based upon two separate processes: (*a*) the conversion, under the influence of acids, of pentoses into furfurol,

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[1] *Ber*, 1883, **16**, 661, 2241, 1884, **17**, 572

[2] *J. d physik-chem*, *Ges*, 1911, **43**, 1190.

[3] Oyerton, *Ber.*, 1893, **26**, 20

[4] *Ann Chim*, 1912, **388**, 165

[5] Meyer and Janny, *Ber.*, 1882, **15**, 1324, 1525, 2778, 1883, **16**, 170.

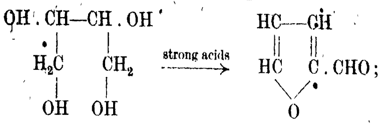
[6] *Loc cit*

[7] Auwers, *Ber*, 1889, **22**, 609

[8] Lieben, *Ann Chim*, 1870, **7**, 236.

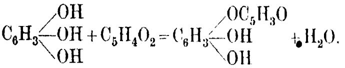
[9] *Ber*, 1884, **17**, 579, 1887, **20**, 833.

[10] *Compt. rend.*, 1891, **112**, 799.



Pentose. Furfurol.

(*b*) the condensation of the furfurol thus formed with a suitable reagent, as, for example, phloroglucinol or orcinol, to yield a characteristically coloured condensation product,



$$C_6H_3\begin{cases}OH\\OH\\OH\end{cases} + C_5H_4O_2 = C_6H_3\begin{cases}OC_5H_3O\\OH\\OH\end{cases} + H_2O.$$

Phloroglucinol + furfurol ⟶ furfurol phloroglucide + water.

As catalytic agent for both hydrolytic split and subsequent condensation, strong hydrochloric acid is usually employed. With phloroglucinol a cherry-red coloration is given, which subsequently changes to a dark-coloured precipitate of the phloroglucide. With orcinol a colour change from red, through violet, to a final blue-green is obtained, followed by separation of a blue green precipitate. The method has been employed by Tollens, Kröber, and Rimbach[1] for the quantitative estimation of pentoses.

The identification of polysaccharides is conducted by means of hydrolysis, using accelerating agents, chiefly mineral acids, with identification of the products of the hydrolytic split.

Amines, amides, nitriles, diazo-, and nitro-compounds.—In the identification and estimation of amines, catalytic methods are not normally employed.

For the qualitative and quantitative estimation of amides and nitriles, hydrolysis of the substance, followed by estimation of the ammonia formed or of the acid produced, is the usual method of procedure. Ordinarily, hydrochloric acid is employed as hydrolytic agent. For difficultly hydrolysable nitriles, Sudborough recommends the conversion of the nitrile to acid amide by digestion with 90 per cent sulphuric acid, followed by conversion to the carboxyl derivative by treatment with nitrous acid. The same treatment is applicable to acid amides. Hydrolysis may also be effected in alkaline solution, in which case, however, precautions must be taken to collect the ammonia evolved.

In the estimation of the diazo-compounds, the use of dilute acids as agents for the liberation of nitrogen is utilised for the aliphatic compounds. The observations made previously as to this reaction apply also to the quantitative estimation, in which, normally, dilute sulphuric acid is the reagent used. With the aromatic diazo-group, a 40 per cent sulphuric acid is employed to decompose the compound, the nitrogen from which may be collected in a Lunge nitrometer.

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[1] *Zeitsch. angew. Chem.*, 1902, **15**, 477.

The nitro-compounds are identified by reduction to the corresponding amine, in which process the possibility of utilising accelerating agents has already frequently been emphasised

Halogen derivatives.—The catalytic process outlined in the section on elementary analysis was originally employed as a method of identification of halogen-substituted organic compounds, and, by the later investigations, was shown to be quantitatively applicable

Esters and glucosides.—Hydrolysis of these compounds with subsequent identification of the products is the normal course of procedure Both acid and alkaline hydrolysis is utilised, according to desire, the principles involved in both being fully set forth in the chapter dealing with hydrolysis

The proteins.—The researches of Emil Fischer on the constitution of the proteins are admirable illustrations of the application of catalysis in organic investigation Fischer showed that, on hydrolysis, the proteins yielded a large number of amino-acids, the individual proteins differing from one another in respect of the number and quantities of the acids obtained by the hydrolytic process, using strong acids as accelerating agent Both monobasic and dibasic amino-acids, as well as diamino-acids, have thus been isolated from the products of hydrolysis, and, from a given protein, as much as 70 per cent of the theoretical yield has been obtained, in the form of different amino-acids, thus showing that the protein molecules consist essentially of conjugations of a large number of amino-acids, schematically representable by the formula

$$\mathrm{COOH\ R\ CH\ NH{-}CO\ R_1\ CH\ NH\ CO\ R_2CH\ NH\ CO\ \ .}$$
$$\mathrm{NH\ CO\,.\,R_{\mathit{n}}\ CH\ NH_2}$$

The approximately quantitative method of estimation of the hydrolysis products may be outlined The protein is hydrolysed by means of sulphuric or hydrochloric acid, generally the latter, in the form of acid of sp gr 1·19 The progress of the hydrolysis is followed by means of the biuret test for protein, the production of a reddish-violet to blue coloration in presence of very dilute copper sulphate solution, and sodium hydroxide After completion of hydrolysis the mixture is concentrated in a vacuum and saturated with hydrogen chloride, whence, on standing, the hydrochloride of glutamic acid separates out The succeeding operation is the esterification of the monoamino-acids in alcoholic solution of hydrogen chloride, several successive operations being necessary in order to overcome the hydrolytic effect of the water produced in the esterification process The subsequent operations consist in the liberation of the free esters from their hydrochlorides and in the separation by fractional distillation, in a vacuum, of the amino-acids into various groups arranged in order of their volatility. To get more effective separation the process involves hydrolysis of the esters and a laborious process of fractional crystallisation of the amino-acids.

Physico-chemical measurements of catalysis in analytical chemistry.—To the reader who has perused the preceding chapters it must have been evident that a considerable number of the reactions therein discussed are readily applicable to the processes of analytical chemistry. Especially in those branches of analysis in which equilibria are present are the normal analytical operations inapplicable, since in the majority of cases these latter are conducted with displacement of the equilibria prevailing. For example, it is obvious that the ordinary analytical processes are frequently not applicable to the determination of the concentrations of hydrolytic products of a given substance in a solution, since they often consist in methods of precipitation, or, in general, of removal of components of the system from the sphere of reaction, which obviously results in displacement of the prevailing equilibrium. In cases such as these the application of physico-chemical methods are invaluable, as may be illustrated by the use made of them by Bredig and by Walker and his co-workers in the examples previously cited in the section on diazoacetic ester decomposition (Chapter XI.). Also it is evident that physico-chemical methods are also widely applicable to a variety of determinations of organic substances, in which the complexity of the materials is a distinct difficulty in the way of ordinary analytical operations, but with which, by a study of their various reactions, in many of which catalytic change is involved, physico-chemical measurement becomes in the most marked degree a useful method of analysis.

The field of reactions involved in a discussion of such measurements extends into both sections of chemical analysis, inorganic and organic. It is preferable, therefore, in order to summarise the various applications of this type, to adopt a classification based upon the agent which is active in the promotion of the catalytic change, to group them therefore according to the part played by hydrogen or hydroxyl ion, water, neutral salt, or gas in promoting the reaction under consideration. In such a way the field of study may be more succinctly covered.

Water.—The rôle of water in various oxidation processes has long been a matter of note. Bergmann's observations that phosphorus oxidises more slowly in dry air than in moist is but one of many early observations of the action of water graphically emphasised by Mrs. Fulhame in her "Essay on Combustion", London, 1794. The views of Mrs. Fulhame on the intervention of water in the oxidation of carbon monoxide were revived by the communication of Dixon to the British Association in 1880, to the effect that the union of carbon monoxide and oxygen only occurred in the presence of water vapour. Baker[1] extended the observations on the accelerating action of water vapour to the combination of ammonia and hydrogen chloride, as well as to the dissociation of the corresponding ammonium salt, to the combination of sulphur trioxide and lime, and to the reaction between illuminated hydrogen and chlorine. Further bibliography on the influence of moisture on chemical change has also been compiled by Mellor and Russell[1] more recently still, and in a more quantitative manner by Tramm[2] It is evident, however, that such positive catalytic influences of water vapour are but little applicable to the purposes of analytical work On the other hand, in a number of reactions in which water functions as an inhibitor, analytical applications are possible

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[1] *J. Chem. Soc.*, 1894, **65**, 611.

In a preceding chapter, in the discussion of esterification processes, it was pointed out that the presence of small quantities of water exhibit extraordinary inhibitory effects on the velocity of esterification in alcoholic solutions This observation furnished Goldschmidt with a method for the determination of small amounts of water in alcohol,[3] consisting in the determination of the velocity of esterification of a 0·1 normal solution of phenylacetic acid in solution in the given example of alcohol, using hydrogen chloride of concentration 0·1 normal as catalytic agent By comparison of the reaction constant obtained with the alcohol under investigation with the values yielded by alcohol containing definite known amounts of water, the aqueous content of the alcohol sample could readily be deduced A similar application of the principle to methyl alcohol is due to Gyr,[4] who employed the same concentrations of esterifiable and catalytic acid as were used by Goldschmidt

A corresponding application of reaction velocity measurements with the analytical determination of water concentrations in alcohols was furnished by the observations of Bredig and Fraenkel[5] on the inhibitory action of water on the catalytic decomposition of diazoacetic ester in alcoholic solutions by aid of acids It was shown that the reaction constant in presence of 0·00909 normal picric acid was as much as $k=0·0524$ in ethyl alcohol dried over calcium, whereas with alcohol containing 0·18 per cent of water the constant had sunk to 0·0401 The observations of Bredig and Fraenkel were subsequently extended by Millar, to whom is due the following table of reaction constants in ethyl alcohol, dehydrated by distillation three times from metallic calcium, in presence of varying concentrations of water, employing 0·00909 normal picric acid as catalysing acid.

Water Concentration in Grm.-mol per Litre.	k.	Water Concentration in Grm.-mols per Litre	k
0·00	0·0570	0·64	0·0175
0·02	0·0534	1·28	0·0115
0·04	0·0467	2·56	0·00645
0·08	0·0424	5·12	0·00435
0·16	0·0334	10·24	0·00491
0·32	0·0256	15·24	0·00760

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[1] *J. Chem Soc*, 1902, **81**, 1272

[2] *Zeitsch. physikal Chem*, 1923, **105**, 356.

[3] Goldschmidt, with Sunde, *Ber*, 1906, **39**, 711, with Udby, *Zeitsch physikal Chem.*, 1907, **60**, 728.

[4] *Ber*, 1908, **41**, 4308

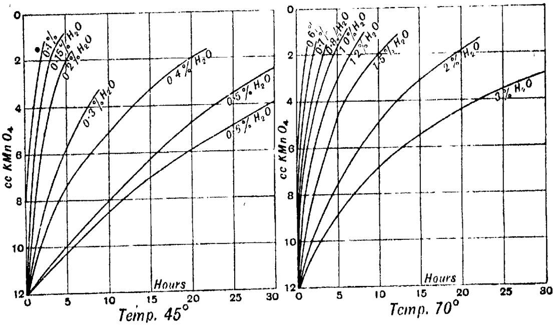
[5] *Ibid.*, 1906, **39**, 1756

The table demonstrates that the reaction velocity passes through a minimum with large concentrations of water, so that the method of estimation is only applicable to small concentrations, the disturbing effect of the corresponding reaction in aqueous solutions making itself felt at higher concentrations. Millar showed that the retarding action of water increased with increasing complexity of the alcohol; thus with methyl, ethyl, and isobutyl alcohols the retardation by 0·32 mol. of water per litre is in the ratio 37 : 55 : 72 per cent.

A further observation of the inhibitory action of water is also due to Bredig, who, in co-operation with Lichty,[1] demonstrated that the decomposition of oxalic acid in presence of concentrated sulphuric acid, according to the equation

$$(COOH)_2 = CO_2 + H_2O,$$

is retarded by the presence of water. It was shown that the influence



Temp. 45°

Temp. 70°

FIG. 27.

of traces of water was so great that it was possible to determine, by means of reaction velocity experiments, concentrations of water which could not be detected by the ordinary analytical methods, or even by determination of the electrical conductivity. Thus the time required to decompose a given quantity of oxalic acid at 25° rose from fifteen minutes in 100 per cent sulphuric acid to two hundred and eighty-five minutes when 0·1 per cent of water was present. With larger concentrations of water the rate of reaction became so slow that it was necessary to carry out the investigations at still higher temperatures. It was then found that at 45° the concentration interval of 0·1-0·6 per cent of water could readily be investigated. Higher concentrations of water were investigated at a temperature of 70°. The accompanying diagrams (Fig. 27) illustrate the retarding influence of the water in such circumstances It must be observed that the presence of sulphates in the acid is not permissible, since they also exert an inhibitory action upon the velocity of reaction

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[1] *Zeitsch. Elektrochem.*, 1906, **12**, 450; *J. Physical Chem.*, 1907, **11**, 225.

Hydrogen ion.—Physico-chemical measurement of hydrogen-ion catalytic activity is mainly confined, in analytical chemistry, to four reactions the inversion of sugar, the velocity of esterification, the rate of ester hydrolysis, and the decomposition of diazo-esters Of all these reactions, the theoretical aspects have previously been discussed Their applications to problems of analysis remain to be mentioned

Naturally, use may be made of any of these reactions for the determination of hydrogen-ion concentration Thus, Walker utilised the measurement of the rate of hydrolysis of esters[1] to measure the hydrolysis of salts yielding acidic products of hydrolysis, and Walker and Aston[2] utilised the inversion of cane sugar to the same end Walker and Wood[3] employed both these reactions to determine the hydrolysis of urea hydrochloride Walker and Cumming[4] applied the diazo-ester decomposition to the general problem of the acid concentrations of amphoteric electrolytes, whilst Spitalsky investigated, in the same manner, the hydrolysis of potassium dichromate[5] The operations are also applicable to biological investigations, as illustrated by the determination by Laborde[6] of the acidity of the gastric juice by measurement of the rate of inversion of cane sugar Hoffmann[7] elaborated the method of estimation, using the inversion of cane sugar and the hydrolysis of methyl acetate

As emphasised in the section on identification of organic compounds, determination of reaction velocity in presence of definite hydrogen-ion concentrations may also be utilised for the analysis of acids and alcohols, as well as of esters

In regard to all such measurements, however, a word of warning is necessary The modifications of reaction velocity brought about by the presence of neutral salts, colloidal material, and the like, limit, strictly, the applicability of this method of analytical investigation

Measurement of the polarisation of sugar solutions before and after inversion by acids is a method for determination of sugar concentrations With cane sugar present alone, the operation is simple, as was demonstrated by Clerget[8] The operation has been applied to the determination of added cane sugar in wine and in condensed milk in the latter case even in presence of milk sugar, since, with a 0 3 per cent hydrochloric acid solution, which is sufficient for the inversion of the cane sugar, the milk sugar is not attacked Polarimetric measurement, before and after inversion, is also employed in determination of mixtures of raffinose and cane sugar, the former of which is inverted about 20 per cent less rapidly than the latter. The raffinose on inversion yields a mixture of the three sugars, glucose, fructose, and galactose, which mixture has, therefore, a greater dextrorotatory power than ordinary invert-sugar.

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[1] *Zeitsch physikal Chem*, 1889, **4**, 319,

[2] *J Amer Chem Soc*, 1895, **17**, 576, 1897, **18**, 120, 693.

[3] *J Chem Soc*, 1903, **83**, 484

[4] *Zeitsch physikal Chem*, 1907, **57**, 578

[5] *Zeitsch anorg Chem*, 1907, **54**, 265

[6] *Gaz méd*, Paris, 1874, **9**

[7] *Zentralbl klin Medicin*, 1889, **10**, 793, 1891, **11**, 521, *Zeitsch. anal Chem Ref*, 1891, **30** 392

[8] *Ann Chim Phys*, 1849 (iii), **26**, 175

Hydroxyl ions.—Of reactions adapted to the determination of hydroxyl-ion concentration, those based on the catalytic influence of alkalis on change of optical rotation are, from the historical point of view, the first to be discussed. Urech[1] showed the dependence, on the strength and concentration of various bases, of the mutarotation of milk sugar, but the operation of a catalytic influence in this case was first pointed out by Ostwald. Consequently, Bredig[2] cites the investigation of Will and Bredig[3] on the action of bases on optical rotatory power in the conversion of hyoscyamine to atropine as the first example of hydroxyl-ion catalysis, with which, moreover, the ion concentration may conveniently be measured, as well as by means of the corresponding racemisation of scopolamine.[4] The reaction occurring is unimolecular and proportional to the hydroxyl-ion concentration, the bases being active in the order of their electrical conductivity. Instances of such measurements could be multiplied, and include the racemisation of tartaric acid,[5] of cotarnine by Dobbie, Lauder, and Tinckler,[6] of amygdalin[7] and of mandelic acid by M'Kenzie and Thompson.[8] According to researches of Trey[9] and Osaka[10] the most accurate method of measuring hydroxyl-ion concentration is in the change of optical rotation of *d*-glucose.

The utility of alkalis in promoting the aldol condensation, as outlined in the chapter on organic synthesis, is also illustrated in the investigations of Koelichen,[11] who showed that the condensation of acetone to diacetone alcohol,

$$2CH_3 . CO . CH_3 \longrightarrow CH_3 . CO . CH_2 . C(OH) . (CH_3)_2,$$

as well as the decomposition of the latter, was promoted by the addition of alkali, and that, as proportionality existed between hydroxyl-ion concentrations and reaction velocity, the change could be employed as a measure of the ionic concentration. The volume change accompanying the reaction was used to determine the reaction velocity, the system under investigation being contained in a dilatometer. The reversibility of the process was particularly well investigated, it being demonstrated that the equilibrium position was unchanged by the presence of th catalyst, and independent of its nature

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[1] *Ber.*, 1882, **15**, 2130; 1883, **16**, 2270; 1885, **18**, 3059.

[2] "Altes u. Neues von der Catalyse", *Biochem. Zeitsch.*, 1907, **6**, 283.

[3] *Ber.*, 1888, **21**, 2777.

[4] Herz, *Chem. Zentr.*, 1911, **15**, 67.

[5] Holleman and Boeseken, *Rec. Pays-Bas*, 1897, **17**, 66; Winther, *Zeitsch. physikal. Chem.* 1906, **56**, 465, 719.

[6] *J. Chem. Soc.*, 1903, **83**, 472; 1904, **85**, 121.

[7] Walker, *ibid.*, 1903, **83**, 472.

[8] *Ibid.*, 1905, **87**, 1019.

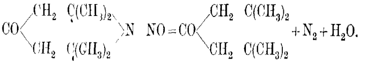
[9] *Zeitsch. physikal. Chem.*, 1895, **18**, 193; 1897, **22**, 424.

[10] *Ibid.*, 1900, **35**, 661.

[11] *Ibid.*, 1900, **33**, 149.

In the saponification of esters, also, a convenient method of determining hydroxyl-ion concentration is evidently available

A recently investigated example of catalytic activity of hydroxyl ions is the decomposition of nitrosotriacetonamine, by alkalis, into phorone and nitrogen, as represented by the equation



It was shown by Francis and Clibbens,[1] and by Francis and Geake,[2]

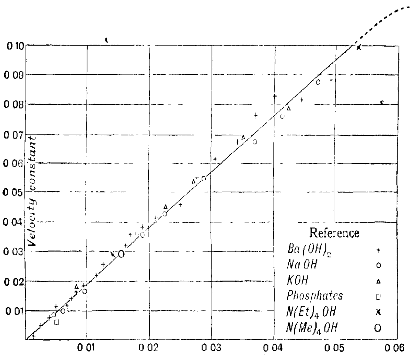


FIG 28

that the unimolecular reaction, occurring in presence of alkalis, was available for the estimation of the concentration of the hydroxyl ions up to the value 0·05 normal Beyond this concentration and as far as 0·3 N/hydroxyl ion the unimolecular constants showed a drift, rendering the method inapplicable for determination of ion concentration in this interval, above which, however, results were again obtained from which ion concentration could be deduced The accompanying diagrams (Figs 28 and 29) illustrate the results obtained The reaction was very conveniently investigated, in the manner employed in the studies of acid catalysis in the diazoacetic ester decomposition, by observation of the nitrogen evolved

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[1] J Chem. Soc, 1912, **101**, 2358

[2] Ibid, 1913, **103**, 1722

The effect of neutral salts on the velocity constant of the decomposition of nitrosotriacetonamine when the concentrations of hydroxyl ions are small[1] is shown in the accompanying diagram (Fig. 30); where the percentage retardations are plotted against the concentration of

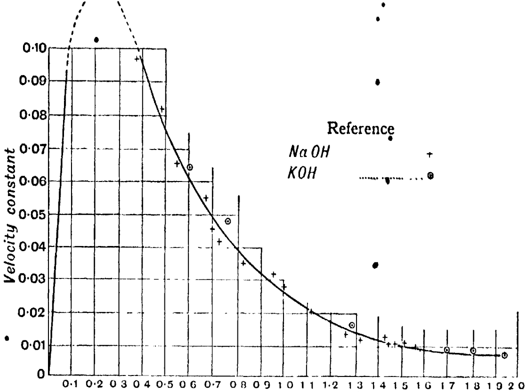

FIG. 29.

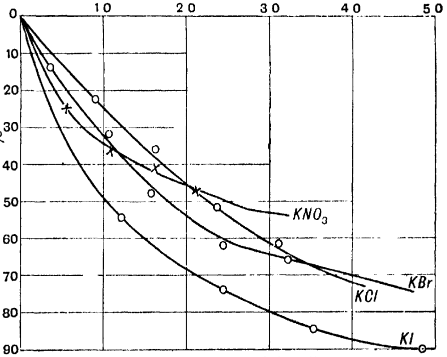

FIG. 30.

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[1] *J. Chem. Soc.*, 1915, **107**, 1651

the neutral salts used. It follows, therefore, that when this method for the determination of alkalinity is used, due allowance must be made in the value of the velocity constant found if neutral salts be present, and the method may thus lose some of its convenience as a method of estimation

The method has also been applied to a number of other nitrosoamines with similar results, typical examples of which are included in the plot of results given in Fig 31

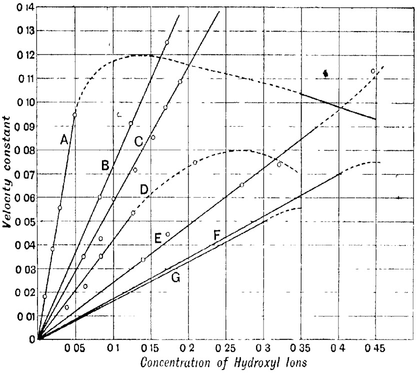

FIG 31

Salts as catalytic agents.—The anions of a number of salts have been shown to function catalytically, and in illustration thereof the researches of Bredig and Walton[1] on the activity of iodides in the decomposition of hydrogen peroxide, and of Bredig and Stern[2] on the influence of cyanides in the condensation of benzaldehyde to benzoin, may be cited

Walton showed that the decomposition of the peroxide in presence of potassium, sodium, and ammonium iodides was a reaction of the first order, the velocity of which was proportional to the concentration of iodide ion With cadmium iodide, which, as is well known, forms a complex anion, the ratio of reaction velocity to concentration of iodide was considerably reduced. Also, the formation of anion complexes with potassium iodide, as, for example, by addition of iodine or mercuric iodide, similarly resulted in a diminution of reaction velocity

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[1] *Zeitsch physikal Chem*, 1904, **47**, 185

[2] *Ibid*, 1905, **50**, 513

In the cyanide reaction Stern showed that the reaction velocity was the same in equal cyanide-ion concentrations, whether from sodium, potassium, or barium cyanides, completely analogous, therefore, to the behaviour of the hydroxides in the saponification of esters. Complex cyanide formation also lowered the reaction velocity, confirming, therefore, the view of anion activity.

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